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Alan P. Kass  
(Print Name)

Date: July 16, 2008

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/alan p. kass/  
(Signature)

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Docket No. 2003US310

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of:

Medhat A. TOUKHY et al.

Art Unit: 1752

Serial No. 10/677,318, filed October 3, 2003

Examiner: SCHILLING, Richard L.

For: **BOTTOM ANTIREFLECTIVE COATINGS**

**ON APPEAL FROM THE PRIMARY EXAMINER TO THE BOARD OF PATENT  
APPEALS AND INTERFERENCES**

**APPELLANTS' BRIEF UNDER 37 C.F.R. § 41.67**

July 16, 2008

Mail Stop Appeal Brief-Patents  
Commissioner for Patents  
P.O. Box 1450  
Alexandria, Virginia 22313-1450

**Attached:**

Serial No. 10/677,318  
Filed: October 3, 2003  
Appellant's Reply Brief under 37 C.F.R. § 41.41

Dear Sir:

The present Reply Brief is submitted in response to the Examiner's Answer dated May 21, 2008.

Appellants need not provide a limiting definition of antireflection coating compositions as the Patent Office thinks they must. Appellants' claims contain, as an element, an antireflective coating composition. Such antireflective coating compositions are defined within appellants' specification (see page 3, line 28 to page 4, line 8; page 7, lines 4 to 15; and page 12, line 15 to page 14, line 5). There is no support for the Patent Office's statement that appellants' argument is unconvincing since there are no examples or disclosure of the use of antireflection layer compositions with only the basic compounds required by the claims.

As appellants have previously stated and shown, the skilled artisan knows what an antireflective coating composition contains. The Patent Office is misconstruing appellants' invention.

To the Patent Office's statement that that the specification does not contain a limiting definition of antireflection coating compositions as containing polymers and absorbers or radiation absorbing polymers, appellants disagree.

On page 12, line 15 to page 14, line 5, appellants demonstrate an antireflection coating composition as containing polymer and absorbers. See page 12, lines 24 to 28 for the antireflective coating composition used to evaluate the bases. The absorber is contained within the polymer. See also the documents incorporated by reference in

appellants' specification at page 4, lines 1 to 8, excerpts of which were included with appellants' brief and copies of which were appended to appellants' brief. It is clear that appellants' antireflection coating compositions are well defined and are well known to the skilled artisan as containing the requisite components.

Appellants' invention is that the antireflective coating composition, which appellants have clearly shown as being understood by one of ordinary skill in the art, also contains a base compound which is not soluble in the solvent of a photoresist composition with which the antireflective coating composition is used.

Thus, it is clear that appellants' invention is not an antireflective coating composition that just contains a basic compound, but an antireflective coating composition that also contains a basic compound.

There is no basis for the arguments of the Patent Office in the paragraph spanning the bottom of page 5 to top of page 6 of the Examiner's Answer. The Patent Office is not providing any factual evidence or scientific reasoning for support. The Patent Office is also misconstruing appellants' invention.

The Patent Office has not set forth a reasonable explanation as to why it believes that the scope of protection provided by that claim is not adequately enabled by the description of the invention provided in the specification of the application. *In re Wright*, 999 F.2d 1557, 1561-62, 27 USPQ2d 1510, 1513 (Fed. Cir. 1993). The Patent Office has not provided any scientific evidence or factual basis for concluding that a person of ordinary skill in the art, using the knowledge available to such a person and the disclosure of appellants' specification could not have made and used the claimed invention. "Nothing more than objective enablement is required, and therefore it is irrelevant whether this

teaching [of how to make and use the full scope of the claimed invention] is provided through broad terminology or illustrative examples.” *Wright, id.*

Here, appellants have provided both broad terminology and illustrative examples that the person having ordinary skill in the art would recognize and understand. The Patent Office has not met the initial burden of proof by advancing reasons or evidence why one of ordinary skill in the art would not be able to make or use the invention as claimed given the broad terminology and illustrative examples provided by appellants.

Thus, contrary to the assertion by the Patent Office that the specification lacks guidance of how to use the compositions, appellants' specification clearly provides more than sufficient guidance in how make and use their antireflective coating compositions that contain a base which is not soluble in a solvent of a photoresist composition used with the antireflective coating composition.

Regarding the Patent Office's statement regarding Hasegawa et al and its reference to appellants' argument on pages 17 to 19 of their brief (see page 6 of the Examiner's Answer), appellants disagree with the Patent Office's statement. As appellants have said in their brief, compositions of Hasegawa et al do not have the components of appellants' invention. Contrary to the Patent Office's statement, appellants' claims are to antireflective coating compositions which also contain base which is not soluble in the solvent of the photoresist composition used with the antireflective coating composition. The Patent Office is misconstruing appellants' invention. Appellants' antireflective coating composition contains polymers and absorbers as those skilled in the art will recognize from appellants' specification. This is clearly demonstrated above. The Patent Office has not provided any factual evidence or scientific reasoning to the contrary.

In the first instance, Hasegawa et al do not disclose antireflective coating compositions. The materials cited in Hasegawa et al are for photoresist compositions, which are different than antireflective coatings. The Patent Office states that "the photoacids of Hasegawa et al absorb imaging radiation which would have reduced reflection (the absorbed radiation would not be available for reflection)." (Page 6 of the Examiner's Answer).

This is incorrect. It is well known that when photoacids are exposed to radiation, they produce acids. The photoacids are not reducing absorption. See, for example, "Hydrogen bonding and cooperativity effects on the assembly of alkyl- and perfluoroalkyl-sulfonyl naphthols: F...F non-bonded interactions," Kowalik, J. et al., *Chem. Commun.*, pp 2007-2008 (1999) at left column, first paragraph, p 2007 (copy attached hereto as Exhibit A (footnotes excluded) (emphasis added)):

**Photoacid generators produce acids upon irradiation.** They are important in the field of polymeric photosensitive systems, as initiators for polymerizations, for crosslinking of oligomers and polymers, for polymer degradation, and for conversion of acid-sensitive functional groups attached to the polymers. Especially important technological applications involve manufacturing of photoresists and UV curing materials. A drawback to common (ionic) photoacid generators is that once incorporated, they usually remain within the polymeric structure, degrading the long-term stability of the polymers.

US 5322765, column 4, lines 47 to 52 (copy attached hereto as Exhibit B (emphasis added)):

Suitable photoacid generators for use in the present invention include radiation degradable acid generators (sometimes known as photoacids). **These photoacids** include metallic and non-metallic onium salts and non-metallic sulfonic acid precursors which **generate strong acids upon exposure to radiation.**

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"Efficiency of Photoacid Generators in Chemically Amplified Resists for 157nm Lithography", Pawloski, A.R., et al, *J. Photopolym. Sci. Tech.*, 15(5), 731-739 (2002) (copy attached hereto as Exhibit C (from left column, page 732) (emphasis added)):

The most common positive-tone chemically amplified photoresists rely on the generation of a strong photoacid by **the decomposition of a photoacid generator (PAG) upon exposure** to catalyze the removal of acid-labile protecting groups from the polymer.

The Patent Office is requested to demonstrate by factual evidence or scientific reasoning that the photoacids of Hasegawa et al could absorb imaging radiation which would have reduced reflection (see page 6, first full paragraph of Examiner's Answer) in a manner that would make any composition of Hasegawa et al an antireflective coating composition like that of appellants.

Hasegawa et al require that the components of its photoresist, including their basic compound, be soluble in the photoresist solvent ("The organic solvent used herein may be any organic solvent in which the base resin, photoacid generator, **and other components are soluble**."; column 21, lines 41 to 43; emphasis added). If the skilled artisan attempts to follow the Patent Office's logic, then where is the solvent for the antireflective coating composition allegedly formed by Hasegawa et al which is different for the solvent of the photoresist composition in Hasegawa et al such that the base in the antireflective coating composition is not soluble in the solvent of the photoresist composition?

There is none and the Patent Office has not demonstrated by factual evidence or scientific reasoning how a skilled artisan would determine how such a solvent is found since Hasegawa et al require that the components in its photoresist be soluble in its solvent (see above).

A skilled artisan would not think the above to be possible on the face of Hasegawa et al or inherently think it possible. "Inherency ... may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient." *In re Oelrich*, 666 F.2d 578, 581, 212 USPQ 323, 326 (CCPA 1981). The only thing the Patent Office has done is provided possibilities.

Where in Hasegawa et al. is the disclosure or teaching to a person having ordinary skill in the art to somehow convert Hasegawa et al.'s photoresist composition to an antireflective coating composition, then use the so-called antireflective coating composition with its photoresist composition, and not have the base soluble in the solvent of the photoresist composition thereof? There is none.

Where is the inherent teaching to a person having ordinary skill in the art to do the same? There is none.

The Patent Office has not made any demonstration thereof through factual evidence or scientific reasoning to support its conclusion. The Patent Office is resorting to impermissible speculation and/or unfounded assumptions to supply deficiencies in Hasegawa et al. The Patent Office has not pointed out where Hasegawa et al. specifically teach each and every element of appellants' invention as arranged in appellants' claims. The same is true for Sato et al and Nishimura et al.

The Patent Office notes that the same compounds (basic compounds) have the same properties including solubility properties (page 7 of the Examiner's Answer). This is incorrect. Appellants' claims require that the base in the antireflective coating composition not be soluble in the solvent of the photoresist composition used with the antireflective coating composition. The Patent Office has failed to demonstrate that Hasegawa et al,

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Sato et al, or Nishimura et al teach such. Hasegawa et al, Sato et al, and Nishimura et al all require that the components in their photoresists be soluble in the solvents used by them:

Hasegawa et al:

**"The organic solvent used herein may be any organic solvent in which the base resin, photoacid generator, and other components are soluble."**; column 21, lines 41 to 43; emphasis added.

Sato et al:

**"[t]he compositions of the present invention are dissolved in solvents dissolving the above-mentioned respective components,** and applied onto supports." paragraph [0111], emphasis added.

Nishimura et al:

**"[t]he radiation-sensitive resin composition of the present invention is prepared as a composition solution by dissolving the composition in a solvent ... ."** see column 51, lines 31 to 33, emphasis added.

The Patent Office is reminded that the standard under § 102 is one of strict identity. "Under 35 U.S.C. § 102, every limitation of a claim must identically appear in a single prior art reference for it to anticipate the claim." *Gechter v. Davidson*, 116 F.3d 1454, 1457, 43 USPQ2d 1030, 1032 (Fed. Cir. 1997). "Every element of the claimed invention must be literally present, arranged as in the claim." *Richardson v. Suzuki Motor Co., Ltd.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). "The identical invention must be shown in as complete detail as is contained in the patent claim." *Ibid*. See also MPEP §2131. None of the documents cited by the Patent Office meet these criteria. "[A]bsence



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from the reference of any claimed element negates anticipation.” *Kloster Speedsteel AB v. Crucible, Inc.*, 793 F.2d 1565, 1571, 230 USPQ 81, 84 (Fed. Cir. 1986), *cert. denied*, 479 U.S. 103 (1987).

Hasegawa et al, Sato et al, and Nishimura et al all fail to disclose an antireflective coating composition that contains a base that is not soluble in the solvent of a photoresist composition. Thus, there can be no anticipation of appellants' claims by those documents.

The Patent Office has not proffered any evidence or scientific reasoning as how the photoresist compositions of the cited documents perform as antireflective coating compositions as claimed by appellants. Additionally, the Patent Office has not shown where an antireflective coating composition containing a base is used with a photoresist composition where the base is not soluble in the solvent of the photoresist composition.

The Patent Office fails to show a teaching of the claimed limitations by the documents that it has cited. “The Patent Office has the initial duty of supplying the factual basis for its rejection. It may not ... resort to speculation, unfounded assumptions[,] or hindsight reconstruction to supply deficiencies in its factual basis.” *In re Warner*, 379 F.2d 1011, 1017, 154 USPQ 173, 178 (CCPA 1967).

The Patent Office has failed to meet the requirements of a Section 102 rejection.

The Patent Office states that the “...claims on appeal define solubility relative to a solvent which is not specified making the solubility of the basic compounds lists in the claims on appeal unspecified.” This is incorrect.

In appellants' claims, as well as their specification, it is stated that the basic compound found in the antireflective coating composition is not soluble in the solvent of the photoresist composition with which the antireflective coating composition is used. See, for example, page 6, lines 21 to 31 and page 9, line 1 to page 11, line 13 of appellants' specification.

The Patent Office appears to be making the requirement that appellants describe everything of their invention in *ipsis verbis* in order to satisfy Section 112. The Patent Office has the burden of making out a prima facie case of non-compliance with this statutory provision by setting forth evidence or reasons why, as a matter of fact, appellants' disclosure would not reasonably convey to persons skilled in this art that appellants were in possession of the invention defined by the claims, including all of the limitations thereof, at the time the application was filed. See, e.g., *In re Wertheim*, 541 F.2d 257, 262-64, 191 USPQ 90, 96-97 (CCPA 1976). The invention claimed does not have to be described in *ipsis verbis* in order to satisfy § 112. It is up to the Patent Office to give reasons why a description not in *ipsis verbis* is insufficient. It appears that the Patent Office is making a Section 112, first paragraph written description rejection.

To meet the initial burden of establishing a prima facie case of unpatentability based on the written description requirement, the Patent Office must "present[ ] evidence or reasons why persons skilled in the art would not recognize in the disclosure a description of the invention defined by the claims." *In re Alton*, 76 F.3d 1168, 1175, 37 USPQ2d 1578, 1584 (Fed. Cir. 1996). Thus, if "the specification contains a description of the claimed invention, albeit not *in ipsis verbis* (in the identical words), then the [Patent Office] ..., in order to meet the burden of proof, must provide reasons why one of ordinary skill in the art would not consider the description sufficient." *Id.* As stated in *Wertheim*, 541 F.2d at 262-265, 191 USPQ at 96-98:

The function of the description requirement is to ensure that the inventor had possession, as of the filing date of the application relied on, of the specific subject matter later claimed by him; how the specification accomplishes this is not material.... It is not necessary that the application describe the claim limitations exactly .... but only so clearly that persons of ordinary skill in the art will recognize from the disclosure that appellants invented processes including those limitations. [Citations omitted.]

A claim does not lack descriptive support merely because “the specification do[es] not contain examples explicitly covering the full scope of the claim language. That is because the patent specification is written for a person of skill in the art, and such a person comes to the patent with the knowledge of what has come before.” *LizardTech, Inc. v. Earth Resource Mapping, Inc.*, 424 F.3d 1336, 1345 76 USPQ2d 1724, 1732 (Fed. Cir. 2005).

Appellants' claims meet the requirements of Section 112 based on the description as provided in their specification.

Regarding the Patent Office's statement that the claims on appeal do not exclude photoresist compositions as in the applied prior art, appellants' claims are to antireflective coating compositions which exclude photoresist compositions. Appellants use photoresist compositions in connection with their antireflective coating composition. This is clear from appellants' claims. The plain language in appellants' claims, read as a whole, indicates that the antireflective coating composition is used with a photoresist composition, it is the antireflective coating composition that contains the base, and the base in the antireflective coating composition is not soluble in the photoresist composition solvent.

The skilled artisan would know what solvents are used in photoresist compositions, contrary to the assertion by the Patent Office on the bottom of page 4 of the Examiner's

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Answer. Appellants need not identify each and every solvent. Breadth is not indefiniteness. *In re Gardner*, 427 F.2d 786, 166 USPQ 138 (CCPA 1970). Also, during patent examination “the PTO applies to the verbiage of the claims the broadest reasonable meaning of the words in their ordinary usage as they would be understood by one of ordinary skill in the art, taking into account whatever enlightenment by way of definitions or otherwise that may be afforded by the written description contained in the applicant's specification.” *In re Morris*, 127 F.3d 1048, 1054-55, 44 USPQ2d 1023, 1027-1028 (Fed. Cir. 1997).

Sufficient guidance to the skilled artisan is provided by appellants in their specification to determine which bases are appropriate for use. See page 10, line 19 to page 14, line 5 of appellants' specification. The Patent Office has not provided any factual evidence or scientific reasoning to the contrary.

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## CONCLUSION

Appellants' claims are clearly enabled and meet all the requirements under 35 U.S.C. § 112. The Patent Office has failed to meet its burden under 35 U.S.C. § 112. In addition, appellants have clearly distinguished their claims from the documents cited by the Patent Office and appellants' claims are patentable over the cited documents. The Patent Office has not met its burden under 35 U.S.C. § 102.

Appellants submit that all pending claims 1 to 9 and 32 to 37 are patentable, the rejections are traversed, and that the present application is in condition for allowance.

Respectfully submitted,

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Exhibit A

# Hydrogen bonding and cooperativity effects on the assembly of alkyl- and perfluoroalkyl-sulfonyl naphthols: F...F non-bonded interactions†

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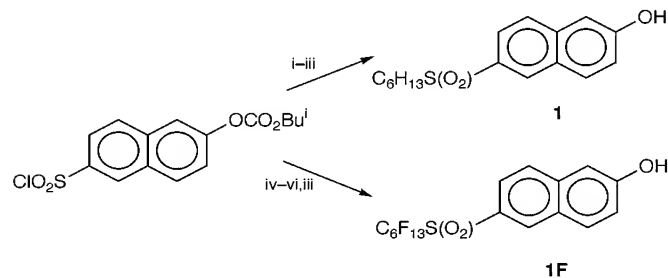
**Important differences in the crystal packing of 6-perfluorohexylsulfonyl-2-naphthol (1F) including  $\pi$ - $\pi$  stacking aromatic interactions and F...F non-bonded contacts, in contrast to its nonfluorinated analog (1), appear to translate into differences between their photophysical properties both in the solid state and in solution.**

Photoacid generators produce acids upon irradiation. They are important in the field of polymeric photosensitive systems, as initiators for polymerizations,<sup>1</sup> for crosslinking of oligomers and polymers,<sup>2</sup> for polymer degradation,<sup>3</sup> and for conversion of acid-sensitive functional groups attached to the polymers.<sup>4</sup> Especially important technological applications involve manufacturing of photoresists and UV curing materials.<sup>5</sup> A drawback to common (ionic) photoacid generators is that once incorporated, they usually remain within the polymeric structure, degrading the long-term stability of the polymers.

A less widely explored approach lies with generators that produce acids only for the duration of the photochemical event, thus allowing for a better control of the ensuing chemistry. Our interest in photoacids stems from the observation that hydroxy aromatics, weakly acidic in the ground state, become strong acids upon photoexcitation.<sup>6</sup> We have established that naphthol derivatives strategically substituted with electron-withdrawing substituents yield significantly stronger acids ('enhanced photoacids') in the excited state.<sup>7</sup> The electron withdrawing efficiency of substituents<sup>8</sup> seems to have a similar effect on the ionization in the excited state, rendering systems substituted with functionalities of large positive Hammett constant ( $\sigma_p$ ) values better photoacids (proton donors).

Since the  $\sigma_p$  value for the pentafluoroethylsulfonyl group is 1.08,<sup>9</sup> versus 0.66<sup>10</sup> for the cyano functionality, we synthesized and tested the 6-perfluorohexylsulfonyl-2-naphthol (1F), and its nonfluorinated analog (1) for comparison. Scheme 1 illustrates our synthetic approach.

The 6-(isobutoxycarbonyloxy)naphthalene-2-sulfonyl chloride, a starting material for both reaction avenues leading to 1 and 1F, was obtained in a two-step process involving masking of the hydroxy group in 6-hydroxynaphthalene-2-sulfonic acid



**Scheme 1** Reagents and conditions: i, Zn, NaOH, H<sub>2</sub>O-dioxane; ii, C<sub>6</sub>H<sub>13</sub>Br, DBU, DMF; iii, LiOH, 50% H<sub>2</sub>O-THF; iv, PPh<sub>3</sub>, PhH; v, NaOEt, C<sub>6</sub>F<sub>13</sub>I, DMF; vi, MCPBA, EtOAc, reflux.

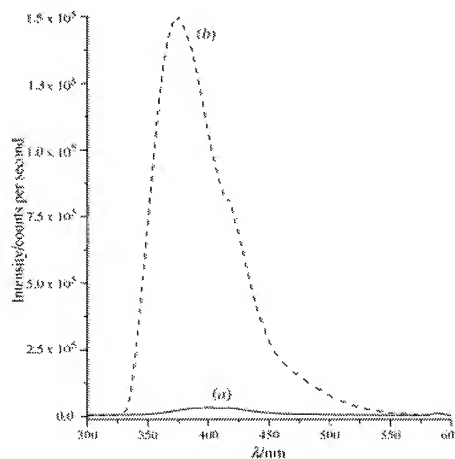
† Atomic numbering schemes and stereoviews for 1 and 1F are available from the RSC web site. See <http://www.rsc.org/suppdata/cc/1999/2007/>

by allowing it to react with isobutyl chloroformate under Schotten-Baumann conditions,<sup>11</sup> followed by a reaction with POCl<sub>3</sub>.<sup>12</sup> Reduction of the acid chloride with zinc metal yielded the corresponding zinc salt of the sulfinic acid, which was alkylated without isolation of the sulfinic acid with *n*-hexyl bromide, using a modified procedure of Mal.<sup>13</sup> The hydroxy group protection in the obtained sulfone was then removed by hydrolysis with LiOH in THF-water to yield 1. Since heteroatom alkylations with perfluoroalkyl iodides proceed *via* a radical-ion chain mechanism,<sup>14</sup> an alternative procedure was developed for the synthesis of 1F. Reduction of the sulfonyl chloride with PPh<sub>3</sub><sup>15</sup> yielded the corresponding thiol, which then reacted smoothly with perfluorohexyl iodide to provide the aryl perfluorohexyl thioether. Oxidation with MCPBA and subsequent deprotection of the hydroxy functionality led to sulfone 1F.

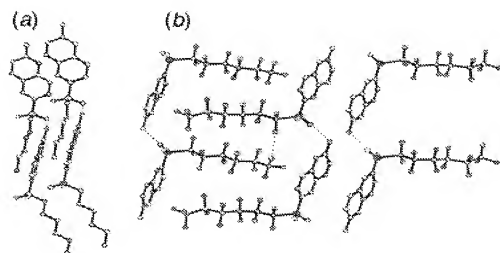
Preliminary studies of the emission spectroscopy of 1 and 1F in aqueous-organic solutions showed considerable differences in the relative intensities of the fluorescence.<sup>16</sup> Emission of the perfluoroalkyl analog was quenched by 40 × in MeOH (Fig. 1).

Similar effects were observed qualitatively in the solid state, using 366 nm radiation from a hand-held laboratory UV-VIS lamp to produce a bright fluorescence of the nonfluorinated sulfone, in contrast with a very low intensity fluorescence of the perfluoroalkyl analog. It was shown, that intermolecular  $\pi$ - $\pi$  interactions effectively quenched the solid state fluorescence, the degree of fluorescence quenching can be used as an indicator of intermolecular  $\pi$ - $\pi$  interactions.<sup>17</sup>

Recent reports from Tung's laboratory indicate that perfluoroalkyl esters of naphthalenecarboxylic acid form aggregates of unknown structure in aqueous organic solvents, leading to formation of excimers upon excitation, and chemical dimerizations as a consequence.<sup>18</sup> Hydrophobic attraction as well as other forces, such as hydrogen bonding,<sup>19</sup> are powerful



**Fig. 1** Emission spectra of (a) 1F and (b) 1 in MeOH. Concentration = 4 × 10<sup>-5</sup> M,  $\lambda_{ex}$  = 295 nm.



**Fig. 2** Packing diagram of (a) **1** and (b) **1F**. For clarity, hydrogen atoms are omitted. The hydrogen bonds and F...F non-bonded interactions are specified by dotted lines.

tools in forming supramolecular assemblies both in solution and in the solid state. Molecular recognition leading to aggregation and nucleation may as a result become productive in generating crystals.<sup>20</sup> Although the dynamics of these systems remains complex, one might assume that the forces that play a role in molecular recognition in self-organized systems in solution would be reflected in the crystal. Following this assumption we determined the crystal and molecular structures of **1**† and **1F**§ (see Fig. 2).

X-Ray analysis reveals that both **1** and **1F** crystallize in monoclinic unit cells, containing four molecules of **1**, and eight molecules of **1F**. The common motif present in both structures is an infinite, intermolecular, linear network of hydrogen bonds OH...OS(O)-. It passes through the crystals in the direction of the *b* axis, making the molecular arrangement supramolecular in nature. Distances are typically 2.78 Å.<sup>21</sup> The differences in the crystal packing are substantial. In the case of **1F** there is a distinct segregation of the well-ordered perfluoroalkane chains from the aromatic rings. The perfluorohexyl chains are nearly parallel. There is a pronounced proximity between the fluorine atom attached to the  $\alpha$  carbon (vs. sulfonyl group) and the terminal CF<sub>3</sub> group of the next molecule. The distance between the corresponding fluorine atoms is 2.85 Å, which positions them within the range of a non-bonded interaction (van der Waals radius for fluorine is 1.47 Å).<sup>22</sup> We believe that the strong electron withdrawing character of the sulfonyl moiety renders the  $\alpha$  fluorine atoms more positive than the terminal ones, effecting a dipolar interaction. This interaction along with the electrostatic repulsion between the  $\pi$ -electrons of the aromatic rings and the fluorine atoms,<sup>23</sup> substantially contribute to the crystal architecture of **1F**. The naphthyl rings in **1F** partially overlap in layers 3.52 Å apart. This value relates well with 3.5 Å (interplanar distance in graphite)<sup>24</sup> and is still smaller than 3.81 Å, where the electronic interaction between the aromatic chromophores was found to exist.<sup>25</sup> The attractive  $\pi$ - $\pi$  interaction is believed to be another element stabilizing the crystal structure of **1F**. By contrast, the planes of the aromatic rings that are positioned parallel to each other in the crystal of **1** are separated by 7.7 Å and are interdigitated with the alkyl chains. There is no interactive proximity between the hexyl chains, and the aromatic chromophores are removed beyond the limit of electron interactions between them.

In summary, three cooperative attractive interactions present in **1F** produce a crystal lattice where a strong chromophore interaction seems to effectively deactivate fluorescence in the solid state. In contrast, the more intense fluorescence of the non-fluorinated analog is attributed to the absence of that interaction. We therefore conclude that similar behavior in solution supports the notion that extensive aggregation of **1F** in MeOH and in water-organic solvent systems is caused by the same attractive interactions as those present in the solid state.

Support of this research from the NSF, grant no. CHE 9727157, is gratefully acknowledged.

## Notes and references

† Crystal data for **1**: C<sub>16</sub>H<sub>20</sub>O<sub>3</sub>S, *M* = 292.38, monoclinic, *a* = 5.6190(2), *b* = 15.8672(6), *c* = 17.1890(7) Å,  $\beta$  = 96.581(2)°, *U* = 1522.4(1) Å<sup>3</sup>, *T*

= 173 K, space group *Cc* (No. 9), *Z* = 4,  $\mu$ (Mo-K) = 0.217 mm<sup>-1</sup>, 4774 reflections measured, 2387 unique (*R*<sub>int</sub> = 0.049) which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.1335 (all data). Single crystals of **1** were recrystallised from Pr<sup>i</sup>OH, mounted on a glass fiber with stopcock grease and placed in the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on *F*<sup>2</sup>.

§ Crystal data for **1F**: C<sub>16</sub>H<sub>7</sub>F<sub>13</sub>O<sub>3</sub>S, *M* = 526.28, monoclinic, *a* = 33.291(1), *b* = 9.9469(2), *c* = 11.4174(3) Å,  $\beta$  = 99.187(1)°, *U* = 3732.3 (2) Å<sup>3</sup>, *T* = 173 K, space group *P2*<sub>1</sub>/*c* (No. 14), *Z* = 8,  $\mu$ (Mo-K) = 0.32 mm<sup>-1</sup>, 18775 reflections measured, 6536 unique (*R*<sub>int</sub> = 0.086), which were used in all calculations. The final *wR*(*F*<sup>2</sup>) was 0.284 (all data). The **1F** was recrystallised from Pr<sup>i</sup>OH, mounted on a glass fiber using stopcock grease and placed in the cold gas stream of the diffractometer. The structure was solved using direct methods and refined by full-matrix least-squares on *F*<sup>2</sup>. CCDC 182/1393. See <http://www.rsc.org/suppdata/cc/1999/2007/> for crystallographic data in .cif format.

- Y. Wei, W. Wang, J. M. Yeh, B. Wang, D. C. Yang and J. K. Murray, *Adv. Mater.*, 1994, **6**, 372.
- J. M. Harvard, M. Yoshida, D. Pasini, N. Vladimirov, J. M. J. Frechet, D. R. Medeiros, K. Patterson, S. Yamada, C. G. Willson and J. D. Byers, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 1225; H. S. Yu, T. Yamashita and K. Horie, *Macromolecules*, 1996, **29**, 1144; K. H. Chae, I. J. Park and M. H. Choi, *Bull. Korean Chem. Soc.*, 1993, **14**, 614.
- S. G. Moon, K. Naitoh and T. Yamaoka, *Chem. Mater.*, 1993, **5**, 1315.
- S. T. Kim, J. B. Kim, C. M. Chung and K. D. Ahn, *J. Appl. Polym. Sci.*, 1997, **66**, 2507; J. P. Chen, J. P. Gao and Z. Y. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 9; H. K. Kim and C. K. Ober, *Polym. Bull.*, 1992, **28**, 33.
- For a recent review see: M. Shirai and M. Tsunooka, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2483 and references cited therein.
- L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A: Chem.*, 1993, **75**, 1; L. G. Arnaut and S. J. Formosinho, *J. Photochem. Photobiol. A: Chem.*, 1993, **75**, 21.
- K. M. Solntsev, D. Huppert, L. M. Tolbert and N. Agmon, *J. Am. Chem. Soc.*, 1998, **120**, 7981; E. Pines, D. Pines, T. Barak, B.-Z. Magnes, L. M. Tolbert and J. E. Haubrich, *Ber. Bunsenges. Phys. Chem.*, 1998, **102**, 511; D. Huppert, L. M. Tolbert and S. Linares-Samaniego, *J. Phys. Chem.*, 1997, **101**, 4602; I. Carmeli, D. Huppert, L. M. Tolbert and J. E. Huppert, *Chem. Phys. Lett.*, 1996, **260**, 109.
- K. Hansch, A. Leo and R. W. Taft, *Chem. Rev.*, 1991, **91**, 165.
- N. V. Kondratenko, V. I. Popov, A. A. Kolomeitsev, E. P. Saenko, V. V. Prezhdo, A. E. Lutsikii and L. M. Yagupol'skii, *Zh. Org. Khim.*, 1980, **16**, 1049.
- D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.
- P. Karrer and P. Leiser, *Helv. Chim. Acta*, 1944, **27**, 678.
- S. Fujita, *Synthesis*, 1981, 423.
- G. Biswas and D. Mal, *J. Chem. Res. (S)*, 1988, 308.
- V. N. Boiko and G. M. Shchupak, *J. Fluorine Chem.*, 1994, **69**, 207.
- S. Oae and H. Togo, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 3802.
- J. Kowalik, C. Clower and L. M. Tolbert, to be published.
- K. Shirai, M. Matsuoka and K. Fukunishi, *Dyes Pigm.*, 1999, **42**, 95.
- C.-H. Tung and H.-F. Ji, *J. Phys. Chem.*, 1995, **99**, 8311; C.-H. Tung and H.-F. Ji, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 2761.
- M. C. Calama, R. Hulst, R. Fokkens, N. M. M. Nibbering, P. Timmerman and D. N. Reinhoudt, *Chem. Commun.*, 1998, 1021; K. A. Jolliffe, M. C. Calama, R. Fokkens, N. M. M. Nibbering, P. Timmerman and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 1998, **37**, 1247; C. J. Kepert, D. Heseck, P. D. Beer and M. J. Rosseinsky, *Angew. Chem., Int. Ed.*, 1998, **37**, 3158; M. Mascal, J. Hansen, P. S. Fallon, A. J. Blake, B. R. Heywood, M. H. Moore and J. P. Turkenburg, *Eur. Chem. J.*, 1999, **5**, 381.
- A. Gavezzotti and G. Filippini, *Chem. Commun.*, 1998, 287; A. Gavezzotti, *Eur. Chem. J.*, 1999, **5**, 567.
- W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, W. A. Benjamin, New York, Amsterdam, 1968, p.16.
- A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.
- N. Hayashi, T. Mori and K. Matsumoto, *Chem. Commun.*, 1998, 1905.
- G. Pimentel and R. Spratley, *Chemical Bonding Clarified Through Quantum Mechanics*, Holden-Day, San Francisco, California, 1969, p. 256.
- H. Langhals, T. Potrawa, H. Nöth and G. Linti, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 478.



## Exhibit B



US005322765A

**United States Patent** [19]

Clecak et al.

[11] **Patent Number:** **5,322,765**[45] **Date of Patent:** **Jun. 21, 1994**[54] **DRY DEVELOPABLE PHOTORESIST COMPOSITIONS AND METHOD FOR USE THEREOF**[75] **Inventors:** Nicholas J. Clecak, San Jose, Calif.; Willard E. Conley, Cornwall, N.Y.; Rane W.-L. Kwong, Wapping Falls, N.Y.; Leo L. Linehan, Walden, N.Y.; Scott A. MacDonald, San Jose, Calif.; Harbans S. Sachdev, Hopewell Junction, N.Y.; Hubert Schlosser, Glashutten, Fed. Rep. of Germany; Carlton G. Willson, San Jose, Calif.[73] **Assignee:** International Business Machines Corporation, Armonk, N.Y.[21] **Appl. No.:** 796,527[22] **Filed:** Nov. 22, 1991[51] **Int. Cl.<sup>5</sup>** ..... G03C 1/72; G03F 7/00[52] **U.S. Cl.** ..... 430/326; 430/270; 430/313[58] **Field of Search** ..... 430/326, 270, 281, 313[56] **References Cited****U.S. PATENT DOCUMENTS**

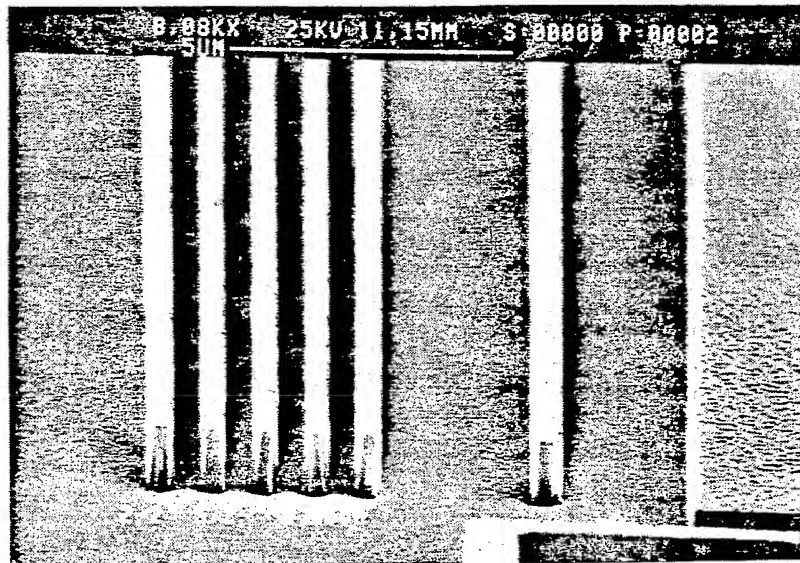
4,371,605	2/1983	Renner	430/280
4,404,272	9/1983	Stahlhofan	430/192
4,613,398	9/1986	Chiong et al.	156/628
4,810,601	3/1989	Allen et al.	430/18
4,863,827	9/1989	Jain et al.	430/145
4,939,070	7/1990	Brunsvold et al.	430/312
5,079,131	1/1992	Thakeray et al.	430/326

**FOREIGN PATENT DOCUMENTS**

204253A	5/1986	European Pat. Off.	G03F 7/26
281182	9/1988	European Pat. Off.	G03F 7/26
282724	9/1988	European Pat. Off.	G03F 7/10
388343A	9/1990	European Pat. Off.	G03F 7/039

**OTHER PUBLICATIONS**Reck et al., *SPIE Regional Technical Conference on Photopolymers* Ellenville, NY 63 (1988), "Novel Photoresist Design Based on Electrophilic Aromatic Substitution."Schellekens et al.; *Proc SPIE* 1086, 220 (1989); "Single Level Dry Developable Resist Systems, Based on Gas Phase Silylation".*Primary Examiner*—Marion E. McCamish*Assistant Examiner*—Rosemary Ashton*Attorney, Agent, or Firm*—John A. Stemwedel; Dale M. Crockatt[57] **ABSTRACT**

Dry developable top surface imageable photoresist compositions which comprise, in admixture, a film-forming aromatic polymer resin activated to electrophilic substitution, an acid catalyzable agent capable of being inserted into the aromatic polymer resin, and a radiation degradable acid generating compound and processes for generating positive tone resist images on substrates therewith.

**23 Claims, 7 Drawing Sheets**

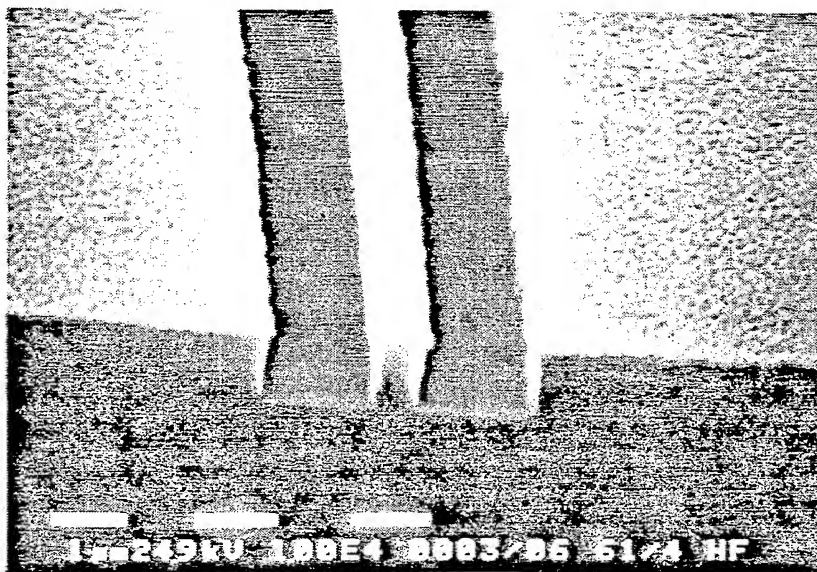


FIG. 1A

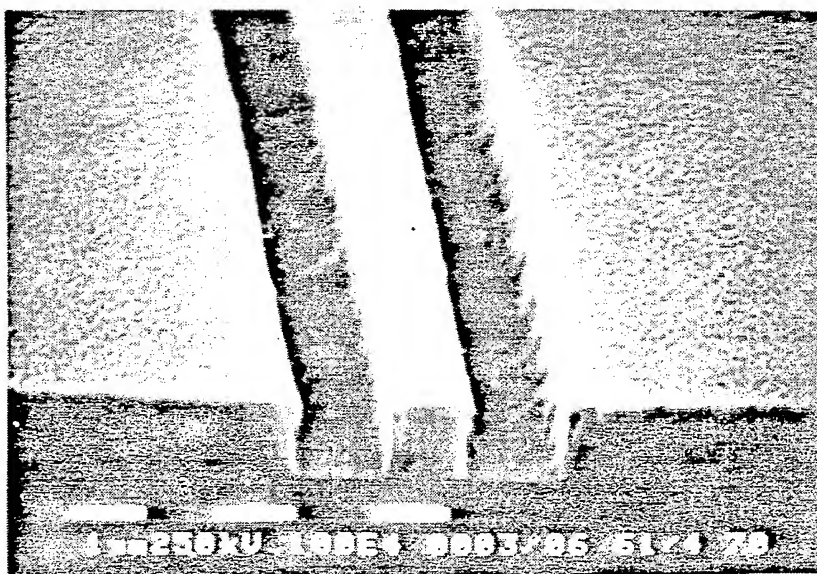


FIG. 1B

FIG. 2

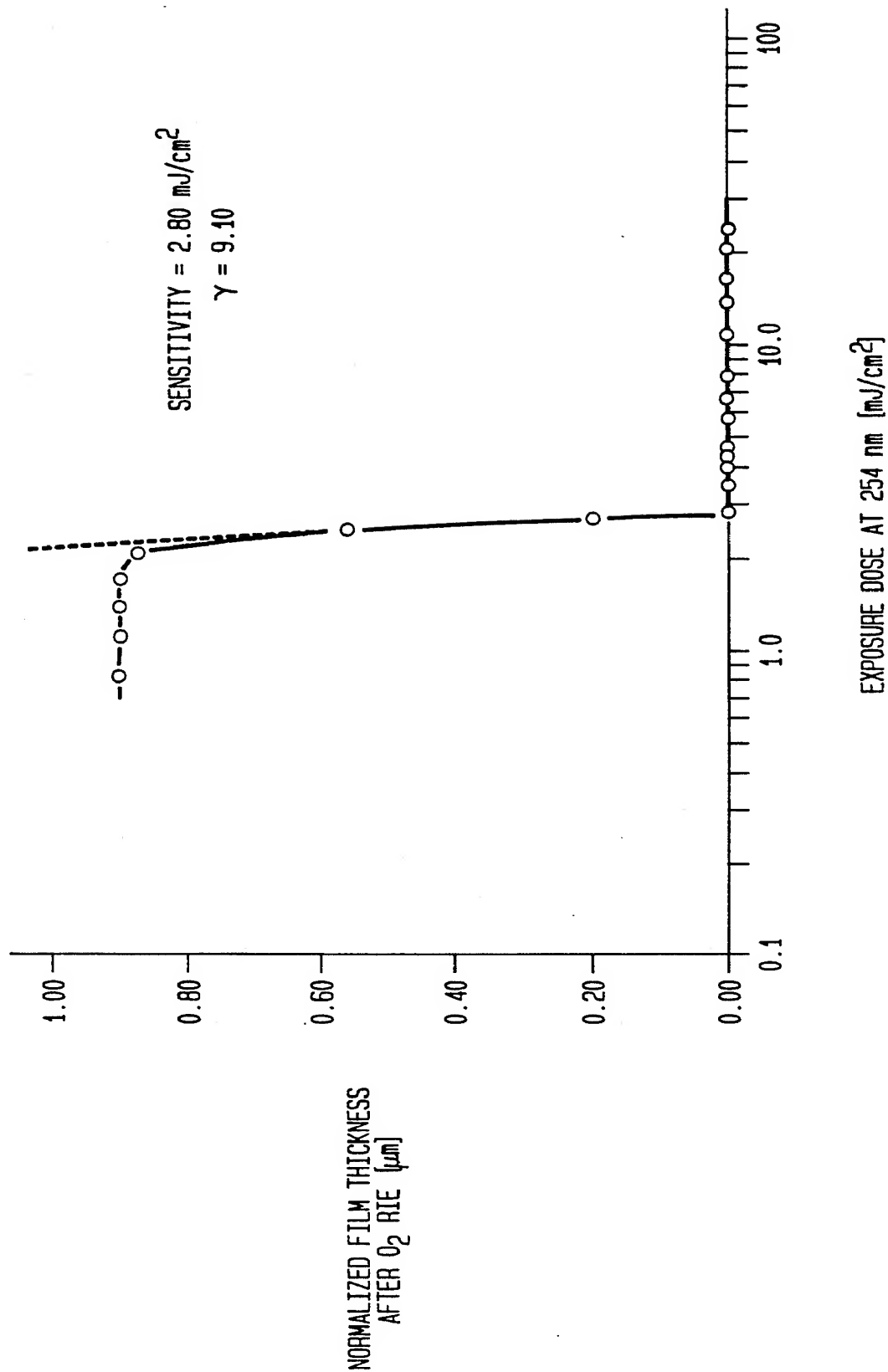
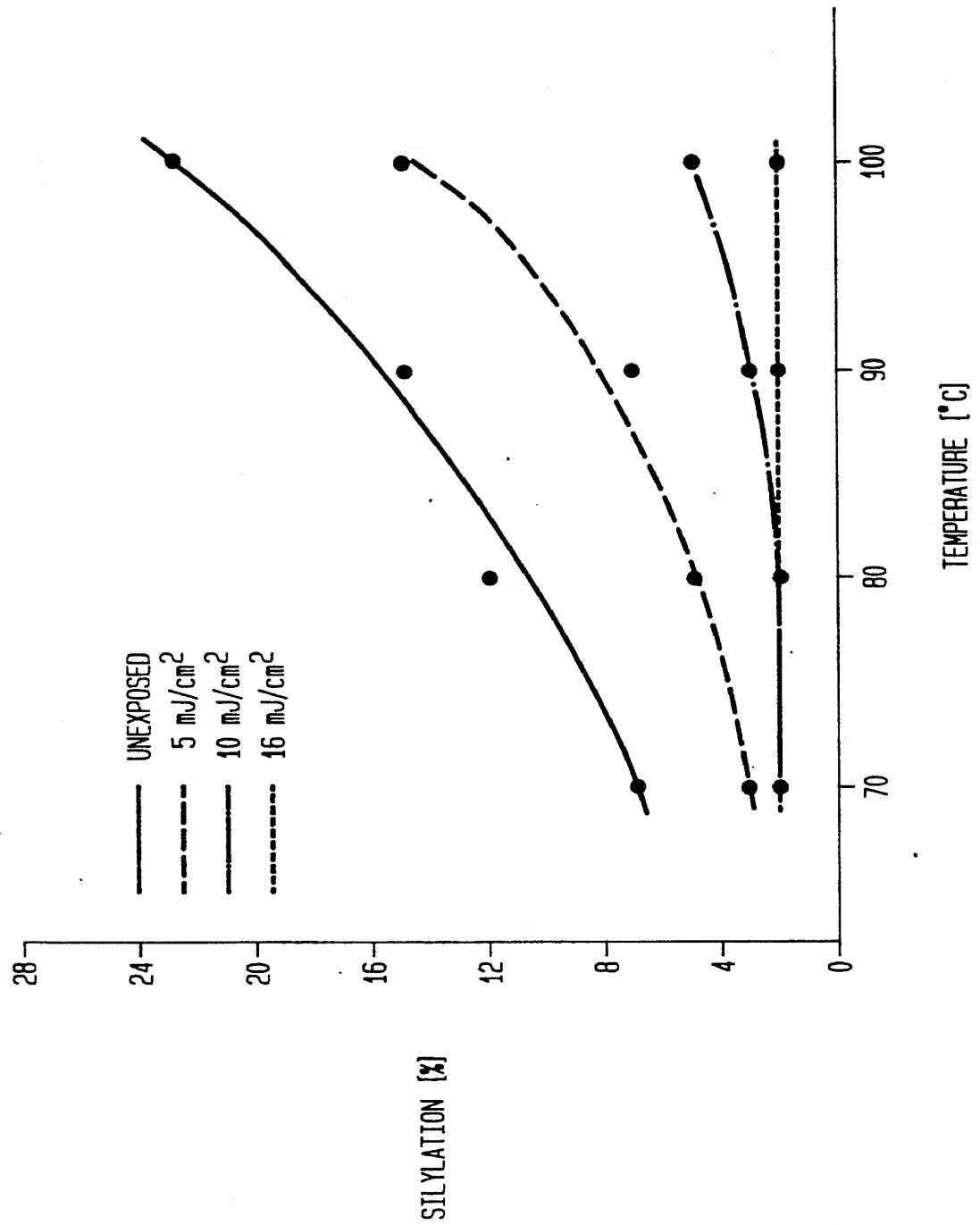


FIG. 3



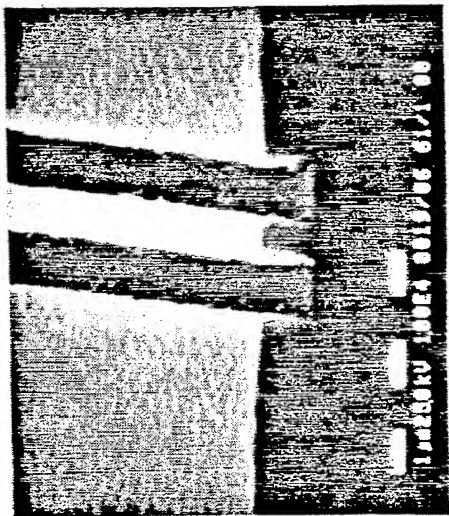


FIG. 4A

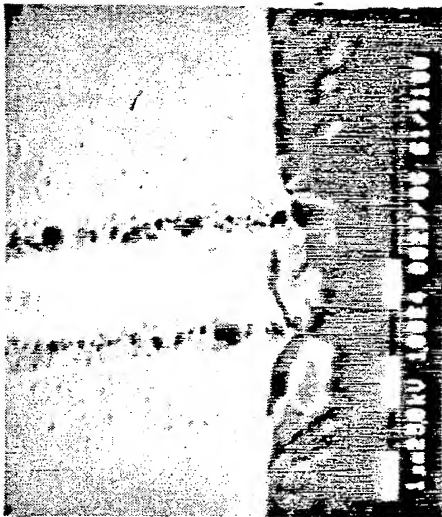


FIG. 4B

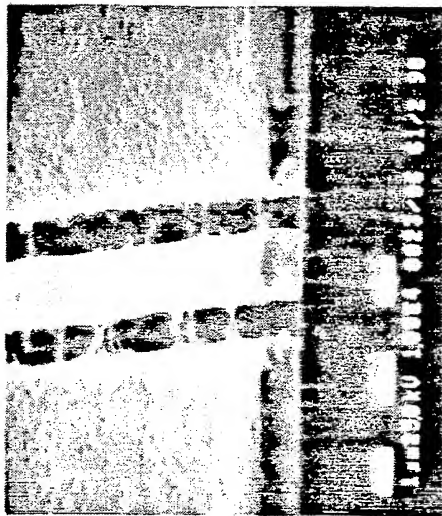


FIG. 4C

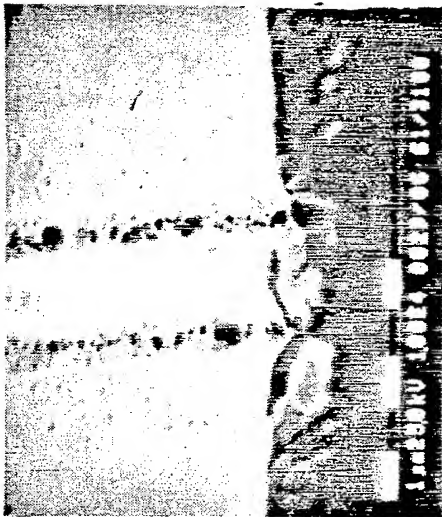


FIG. 4D

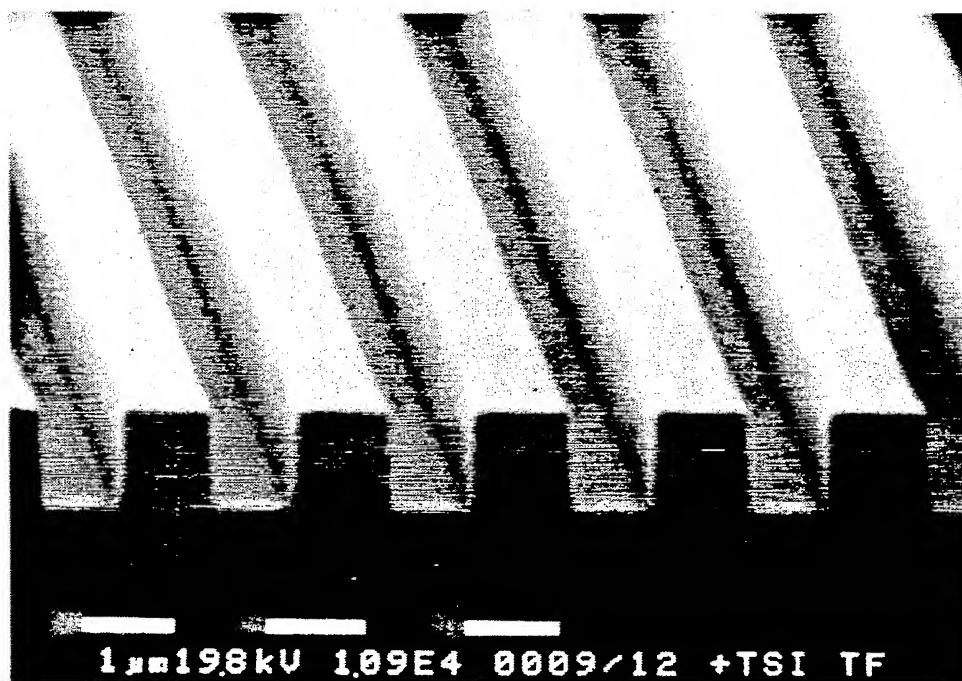


FIG. 5

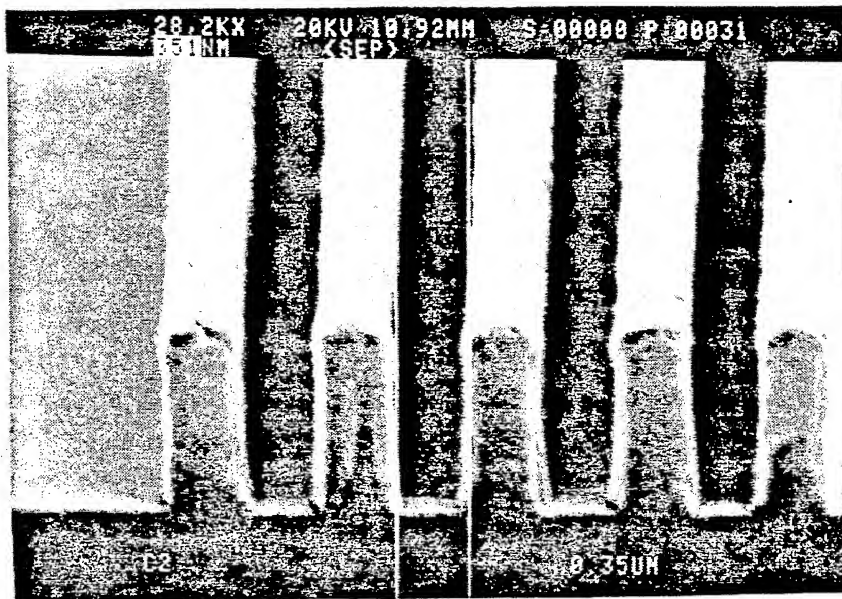


FIG. 6A

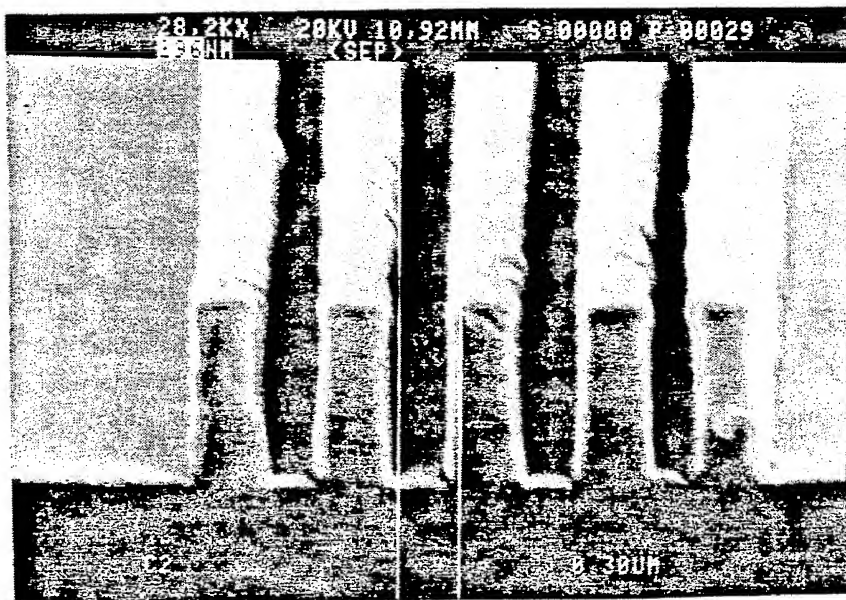


FIG. 6B



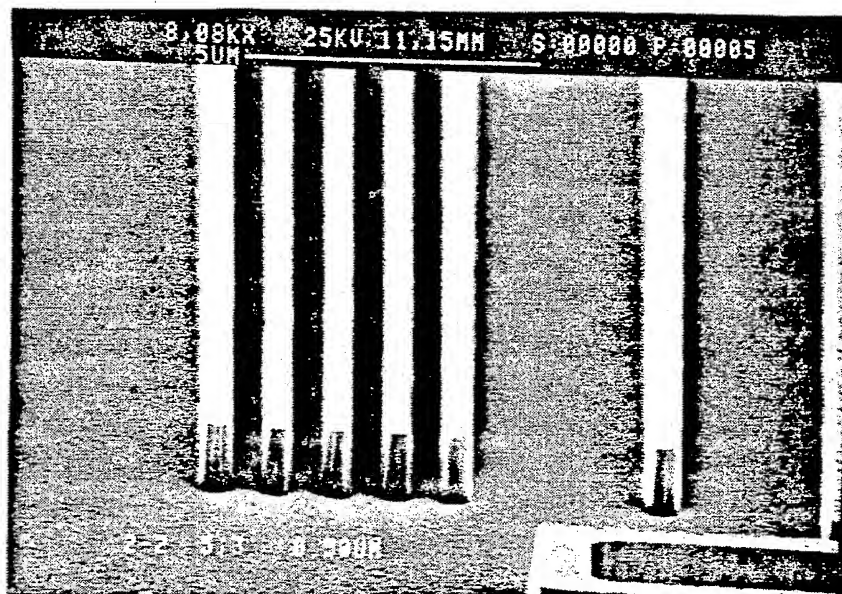


FIG. 7A

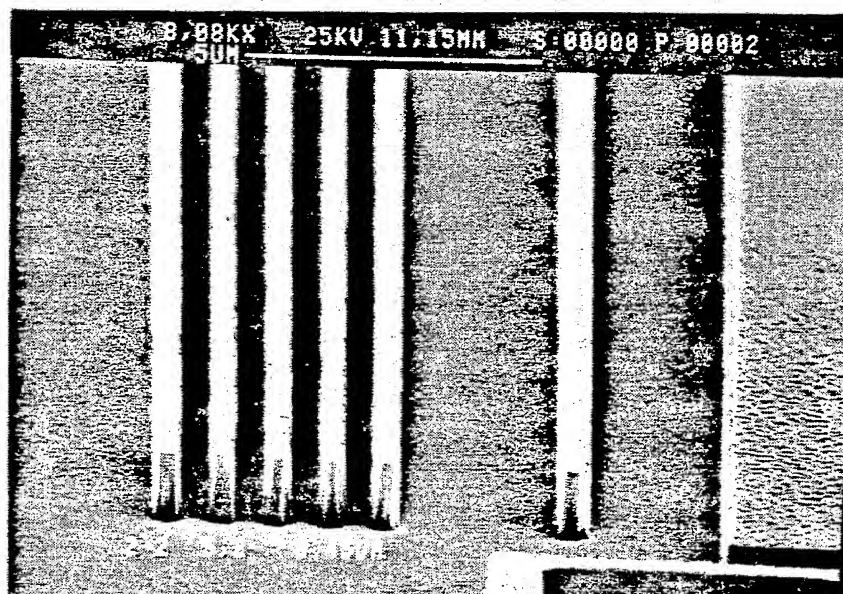


FIG. 7B

# DRY DEVELOPABLE PHOTORESIST COMPOSITIONS AND METHOD FOR USE THEREOF

## FIELD OF INVENTION

The present invention relates to processes for forming lithographic patterns with dry-developable, top surface imageable photoresist compositions.

## BACKGROUND OF THE INVENTION

There has been a continuing desire in the electronics industry to obtain higher circuit density in microelectronic devices. To achieve the higher degree of integration necessary to meet the ground rules for such devices, lithographic techniques have been subjected to improvements which enhance the resolution of lithographic patterns in photoresist films.

Aqueous base developable photoresist compositions which crosslink through electrophilic aromatic substitution have been disclosed in Reck et al., *SPIE Regional Technical Conference on Photopolymers*, Ellenville, N.Y., 63 (1988). Such formulations are characterized by having 3 structural components which include (a) an aromatic moiety, such as poly(4-hydroxystyrene) or novolak, which is susceptible to electrophilic aromatic substitution and allows for development under ionizing conditions, (b) a stable substance which is capable upon reaction with acid, of generating an electrophile, viz., a carbocationic species whose precursor is the acetate of an aryl methylol, and (c) a photo-acid generator which is an onium salt such as triphenylsulfonium hexafluoroantimonate. Upon exposure latent images are formed consisting of a strong acid dispersed in the exposed areas of the resist film. When the film is baked briefly after exposure, the acid cleaves the acetate group of the latent electrophile to produce a benzylic carbocationic species which reacts immediately with the surrounding phenolic resin to form new carbon-carbon bonds. Such formation of new carbon-carbon bonds results in an increase in molecular weight of the resin or its crosslinking, thereby drastically altering its solubility properties. Subsequent development in dilute base affords a negative-tone image of the mask. (Systems which included novolak resins were said to exhibit an unacceptable high optical density in deep UV).

In Schellekens et al., *Proc. SPIE* 1086, 220 (1989), single layer resist systems are provided that involve the gas phase silylation and dry development of diazoquinone novolak resists and poly(vinylphenol) resists in the novolak case a novolak identified as AZ-Protective Coating was used and 2,6-bis(hydroxymethyl)-4-*t*-butyl-1-hydroxybenzene was used as a crosslinking agent and diphenyliodonium hexafluorophosphate was used as the deep UV sensitizer. In the case of the poly(vinylphenols), hexamethoxymethylmelamine was used as the crosslinker and 2(4-phenylphenyl)-4,6-bis(trichloromethyl)-s-triazine was used as the sensitizer. In contrast to previously known esterification crosslinking schemes, the authors of this paper took as the position that the crosslinking both in the case of the novolak species and in the case of the poly(vinylphenols) occurs due to a transesterification mechanism. The crosslinking sites are the hydroxy groups on the polymer chain. This paper further discloses the silylation of the resists using both hexamethyl disilazane and trimethylsilyldimethylamine as silylating agents.

U.S. Pat. No. 4,613,398 to Chiong et al. is directed to methods for formation of etch resistant resists through the preferential permeation of organometallic materials into the differentially exposed polymeric resist materials. In certain embodiments, the differential permeation is achieved through the crosslinking of the polymer molecules to increase the molecular weight of the polymer and reduce its permeability. Typical of the photocrosslinkable polymers are those which contain functional groups such as hydroxy, carbonyl, phenol, amine and imide NH. These polymers include novolak resins, resoles, epoxides, and polymers containing azido groups and polyvinylphenol additionally crosslinking may be through polyfunctional monomers and prepolymers containing double bonds and epoxy groups.

U.S. Pat. No. 4,810,601 to Allen et al. is concerned with the formation of top surface images in resist films that transfers the image to only the top surface of the film so that the subsequent treatment with organometallic reagent occurs only in the top fraction of the film which is more permeable or more reactive to the organometallic reagent giving a structure which is equivalent to a bi or multilayer system. That disclosure is directed primarily to those materials which have recurrent acid labile pendent groups that when released from the polymer chain provide sights for reaction with the organometallic material.

U.S. patent application Ser. No. 07/735,420, filed Jul. 25, 1991 to Allen et al., is directed to methods for converting chemically amplified photoresist systems to a top surface imaging resist system by the incorporation of an opaquing dye in the photoresist composition to prevent the passage of imaging radiation through a substantial portion of the film and treating the imaged film with a silylating agent and dry developing such treated film to form negative tone resist images.

## SUMMARY OF THE INVENTION

The present invention relates to processes for generating positive tone resist images on a substrate comprising the steps of:

(a) coating the substrate with a film comprising (i) a film-forming aromatic polymer resin having functional groups which activate said resin to stabilize said resin to electrophilic aromatic substitution, (ii) an acid catalyzable crosslinking agent which forms a carbonium ion upon reaction with acid, and (iii) a radiation degradable acid generator which is adapted to absorb imaging radiation, such that, upon crosslinking, said composition is more highly densified and is less permeable to the absorption of an organometallic reagent in the crosslinked regions than it is in the non-crosslinked regions;

(b) imagewise exposing of the film to mid or deep UV radiation to cause densification of the resin in the exposed portion of the film;

(c) contacting said film with an organometallic reagent to absorb the organometallic agent in such more permeable unexposed areas; and,

(d) etching the film with reactive ions to yield a positive resist pattern.

In the preferred embodiment of the invention the carbonium ion formed is a benzyl carbonium ion.

In an alternative embodiment of the present invention, an aromatic dye may be included in the composition.

A more thorough disclosure of the present invention is presented in the detailed description which follows and in the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 are photomicrographs showing images made by the process of the invention.

FIG. 1A shows images made by the process of the invention and after a brief dip in hydrofluoric acid solution.

FIG. 1B shows images made by the process of the invention before a brief dip in hydrofluoric acid solution.

FIG. 2 is a plot of sensitivity and contrast using the process of the invention.

FIG. 3 is a plot showing percent silylation as a function of process temperature.

FIG. 4 is a comparison of image degradation as a function of silylation temperature.

FIG. 4A is a photo micrograph showing images silylated at a temperature of 70 degrees C.

FIG. 4B is a photo micrograph showing images silylated at a temperature of 80 degrees C.

FIG. 4C is a photo micrograph showing images silylated at a temperature of 90 degrees C.

FIG. 4D is a photo micrograph showing images silylated at a temperature of 100 degrees C.

FIG. 5 shows an image profile made using a dyed photoresist.

FIG. 6 shows deep UV imaging of a photoresist using monomeric crosslinking agents.

FIG. 6A is a photo micrograph showing 0.35 micrometer images.

FIG. 6B is a photo micrograph showing 0.30 micrometer images.

FIG. 7 shows i-line imaging of a photoresist using monomeric crosslinking agents.

FIG. 7A is a photo micrograph showing 0.50 micrometer images.

FIG. 7B is a photo micrograph showing 0.45 micrometer images.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to processes for generating positive tone resist images on a substrate comprising the steps of:

(a) coating the substrate with a film comprising (i) a film-forming aromatic polymer resin having functional groups which activate said resin to electrophilic aromatic substitution, (ii) an acid catalyzable crosslinking agent which forms a carbonium ion upon reaction with acid, and (iii) a radiation degradable acid generator which is adapted to absorb imaging radiation, such that, upon crosslinking, said composition is more highly densified and is less permeable to the absorption of an organometallic reagent in the crosslinked regions than it is in the non-crosslinked regions;

(b) imagewise exposing of the film to mid or deep UV radiation to cause crosslinking of the resin in the exposed portion of the film;

(c) contacting said film with an organometallic reagent to absorb the organometallic agent in such more permeable unexposed areas; and,

(d) etching the film with reactive ions to yield a positive resist pattern.

In the first step of the process of the present invention, a suitable substrate such as silicon, silicon oxide, silicon nitride or gallium arsenide is coated with a film comprising the resist composition which is dissolved in a suitable organic solvent.

The aromatic polymer resin has functional groups which are preferably phenolic hydroxy groups, which activate the aromatic ring to electrophilic aromatic substitution. Typically such aromatic polymer resins will be activated ring systems such as polyhydroxystyrene or novolak resins. These materials include copolymers thereof and should be considered to comprise poly(hydroxystyrene), poly(hydroxystyrene-co-*t*-butyloxycarbonyloxystyrene), poly(hydroxystyrene-co-hydroxymethylstyrene), poly(hydroxystyrene-co-acetoxymethylstyrene) alkyl substituted polyvinyl phenols and novolak resins such as cresol novolak, ethylphenol novolaks, xylenol novolaks, etc.

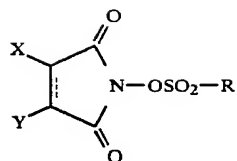
The acid catalyzable crosslinking agent is carbonium ion precursor. The preferred carbonium ions are benzylic carbonium ions, that is, phenyl methyl in form, and more than one carbonium ion site may be present on the precursor. Typical functional groups which react with acid to form carbonium ions are acetate groups on benzyl acetate type structures. The aromatic ring may be part of a polymer chain and be monomeric and may contain substituents which promote the formation and stabilization of the carbonium ion. The substituents must however be compatible with the imaging and stability characteristics of the final resist formulation. Preferred substituents include hydroxy ( $-\text{OH}$ ), lower alkyl (preferably  $-\text{CH}_3$ ), and substituted lower alkyl (preferably  $-\text{CH}_2\text{OAc}$ , where OAc is acetate).

The crosslinking agents include poly-functional aromatic polymers which react with acid to form benzyl carbonium ions. The polymers need not have functional precursor groups on each aromatic ring. The preferred polymer structures are poly acetoxymethylstyrene and copolymers thereof. The most preferred copolymers are poly(acetoxymethylstyrene-co-hydroxystyrene) polymers. Para orientation is preferred and the ratio of hydroxystyrene to acetoxymethyl styrene is 4 to 1.

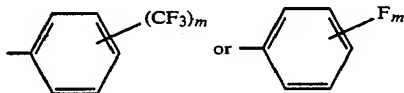
The useful monomeric crosslinking agents are of the form of diacetoxymethyl phenolic monomers. It has been found that having the acetoxymethyl groups in the ortho position with respect to a phenolic hydroxy group promotes stabilized carbonium ions. The preferred monomeric carbonium ion precursors include 2,6-diacetoxymethyl-*p*-cresol, 2,6-diacetoxymethylphenol, 2,2',6,6'-tetracetoxymethyl-Bisphenol A and trisacetoxymethylstyrene.

Suitable photoacid generators for use in the present invention include radiation degradable acid generators (sometimes known as photoacids). These photoacids include metallic and non-metallic onium salts and non-metallic sulfonic acid precursors which generate strong acids upon exposure to radiation. Typical of the onium salts are diaryliodonium and triarylsulfonium salts. These photoacids may include diphenyliodonium hexafluoroarsenate, di(*t*-butylphenyl)iodonium hexafluoroarsenate, diphenyliodonium hexafluoroantimonate, diphenyliodonium triflate, di(*t*-butylphenyl)iodonium triflate, triphenylsulfonium hexafluoroantimonate, tri(*t*-butylphenyl)sulfonium hexafluoroantimonate, triphenylsulfonium hexafluoroarsenate, tri(*t*-butylphenyl)sulfonium hexafluoroarsenate, triphenylsulfonium hexafluorophosphate, tri(*t*-butylphenyl)sulfonium hexafluorophosphate, triphenylsulfonium triflate and tri(*t*-butylphenyl) sulfonium triflate.

Among the non-metallic sulfonic acid precursors which generate strong acids upon exposure to radiation are N-sulfonyloxyimides of the form



where R is selected from the group consisting of  $-\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_2\text{H}$ ,  $-(\text{CF}_2)_n-\text{Z}$  where  $n=1$  to  $4$ , where Z is H, alkyl, aryl,



where  $m=1$  to  $5$ , where X any Y either (1) form a cyclic or polycyclic ring which may contain one or more hetero atoms, (2) form a fused aromatic ring, (3) may be independently H, alkyl or aryl, (4) may be attached to another sulfonyloxyimide-containing residue, or (5) may be attached to a polymeric chain or backbone.

The film may also comprise an aromatic dye which functions to absorb substantially all imaging mid and deep UV radiation incident on the film during the process before it reaches the substrate. The imaging mid and deep UV radiation used to process the present invention preferably has a wave length of from about 200 to about 370 nm. Suitable dyes include phenoxymethyl anthracene, anthracenemethanol, 9,10-diphenylanthracene, and phenanthracene and biphenyl derivatives.

In the second step of the process of the present invention, the film is imagewise exposed to mid or deep UV radiation to densify the aromatic polymer in the exposed region of the film. Suitable radiation sources include various arc lamps as mercury, deuterium or excimer laser source.

In the third step of the process of the present invention, the film is contacted with an organometallic agent in liquid or gas phase. The preferred metallic portions of the organometallic agent comprise silicon, tin, germanium and titanium. Preferred organometallic compounds are organosilicon and organostannyl compounds including, for example dimethylaminotrimethylsilane, hexamethyldisilazane, trimethylsilylchloride, trimethylstannylchloride and 1,1,3,3,5,5-hexamethylcyclotrisilazane. Other organometallic agents will be known to those skilled in the art.

The un-crosslinked portions of the resists film absorb the organometallic compound to provide the film with resistance to  $\text{O}_2$  reactive ion etching.

The final step of the process of the present invention involves reactive ion etching of the film to yield positive tone dry-developed images etching techniques and etching agents and equipment are well known in the art. In the present invention it is preferred that the etching plasma be an  $\text{O}_2$  plasma.

The following examples are detailed descriptions of methods of preparation and use of the process of the present invention. The detailed preparations fall within the scope of, and serve to exemplify, the more generally described methods set forth above. The examples are presented for illustrative purposes only, and are not intended to restrict or limit the scope of the invention.

#### EXAMPLE 1

2.0 g of poly (*p*-hydroxystyrene-co-*p*-acetoxymethylstyrene) having approximately 8 *p*-hydroxystyrene groups to 2 *p*-acetoxymethylstyrene groups and 0.10 g of triphenylsulfonium hexafluoroarsenate were formulated as a photoresist having 18 weight % of solids in propylene glycol monomethyl ether acetate (PMA). This photoresist mixture was spin coated at 4,000 rpm onto silicon wafers to form a coating 1.0  $\mu\text{m}$  thick and the coated wafers were baked at 90° C. for four minutes on a hot plate. The coated wafers were exposed to 16 mJ/cm<sup>2</sup> of deep UV radiation using a Perkin-Elmer Micraline 500 operating in the UV-2 mode. The exposed wafers were baked on a hotplate for 3 minutes at 120° C. The exposed wafers were then silylated for 5 minutes at 70° C. using 200 Torr of dimethylaminotrimethylsilane. The silylated wafers were transferred to a Plasma-Therm parallel plate reactive ion etch tool for  $\text{O}_2$  plasma development of the relief image. The etching conditions were as follows: 150 watts RF power, 40 SCCM  $\text{O}_2$ , 20 mTorr and etch time of 30 minutes. The relief image generated in this Example is shown in FIG. 1.

The sensitivity and contrast of this formulation at 254 nm were determined to be approximately 3 mJ/cm<sup>2</sup> and 9 respectively as are shown in FIG. 2.

#### EXAMPLE 2

The amount of silicon incorporated into a resist film is strongly influenced by the silylation temperature. This was studied by using IR spectroscopy to measure silicon uptake as a function of silylation temperature and exposure dose. In this Example the resist formulation of Example 1 was spin coated onto NaCl substrates and baked. The coated substrates were divided into four sets, the 1st set was exposed to 5 mJ/cm<sup>2</sup>, the 2nd set was exposed to 10 mJ/cm<sup>2</sup>, the 3rd set was exposed to 16 mJ/cm<sup>2</sup>, and the 4th set was unexposed. The wafers were baked at 120° C. for 4 minutes and were silylated with dimethylaminotrimethylsilane for 5 minutes at 200 Torr at various reaction temperatures. FIG. 3 provides plots showing that the percent silylation (as determined by IR spectroscopy) increases with temperature and decreases with UV exposure dose.

#### EXAMPLE 3

This Example shows the influences that silylation temperature has on the quality of the developed relief image. In this study the formulation was coated onto 5 inch silicon wafers and was processed as described above in Example(s) 1 and 2. The process conditions were held constant except for changes in the silylation temperature which was varied from 70 (FIG. 4A) to 100° C. (FIG. 4D). As may be seen from FIG. 4, the higher the temperature during silylation, the greater the degradation of the quality of the relief image.

#### EXAMPLE 4

A top surface imageable resist was prepared by adding 9-phenoxymethylanthracene, an opaquing agent, to the resist composition of Example 1. The composition of the system was as follows: 17% (wt/wt) poly(*p*-hydroxystyrene-co-*p*-acetoxymethylstyrene), 0.9% (wt/wt) 9-phenoxymethylanthracene, 0.9% (wt/wt) triphenylsulfonium trifluoromethylsulfonate, and 81.2% (wt/wt) propylene glycol monomethyl ether acetate (PMA). This photoresist composition was spin

coated at 3000 rpm onto silicon wafers to form a coating 0.8  $\mu\text{m}$  thick. The coated wafers were baked at 90° C. for 1 minute and were then exposed with 3.5 mJ/cm<sup>2</sup> of deep UV light using a 1X Ultratech step-and-repeat tool (model X-248E) operating at 248 nm with a 7 nm wide band pass filter. The exposed wafers were then silylated for 2 minutes at 70° C. using 200 Torr of dimethylaminotrimethylsilane in a MONARCH single wafer silylation tool. The silylated wafers were transferred to a Materials Research Corporation magnetically enhanced plasma etch tool (model #MIE 710). The etching conditions were as follows: 1 kW RF power, 10 SCCM O<sub>2</sub>, 1.0 mTorr, and an etch time of 1.2 minutes. The wafer was rinsed with 6:1 buffered HF, followed by water to remove a small amount of substrate residue. FIG. 5 shows the relief image generated in this process.

#### EXAMPLE 5

Preparation of 2,6-diacetoxymethyl-*p*-cresol was accomplished in a quantitative manner by reaction of *p*-cresol with 2 equivalents of formaldehyde to form di-2,6-hydroxymethyl *p*-cresol which was further treated with acetic anhydride and sulfuric acid in acetic acid to form the diacetate(diester).

This diacetate was compounded into a photoresist formulation such that there was 14.40% (w/w) poly(*p*-hydroxystyrene), 1.00% (wt/wt) 2,6-diacetoxymethyl-*p*-cresol, 1.15% (w/w) 9-anthracenemethanol, 81.99% (w/w) propylene glycol methyl ether acetate and 1.44% (w/w) MDT (trifluoromethylsulfonyloxy-bicyclo[2.2.1]-hept-5-ene-2,3-dicarboximide), the non-metallic sulfonic acid precursor of U.S. patent application Ser. No. 07/322,848 filed Mar. 14, 1989, the disclosure of which is incorporated into the present application. This photoresist formulation was spin coated onto silicon wafers to form a 1.1  $\mu\text{m}$  thick coating. The coated wafers were baked at 90° C. for 1 minute and were then exposed with 4.0 mJ/cm<sup>2</sup> of 248 nm light using a 0.37 NA CANON excimer step and repeat tool. The wafers were post-exposed baked on a 110° C. hot-plate for 12 seconds. The wafers were then silylated for three minutes at 60° C. using 100 Torr dimethylaminotrimethylsilane in a MONARCH 150 single wafer silylation tool. The silylated wafers were etched in an Applied Materials AME5000 magnetically enhanced plasma etch tool. Etching conditions were as follows: 500 w RF power, 20 SCCM O<sub>2</sub>, 50 mTorr, 60 Gauss for 90 seconds. Etch residue was removed from the wafers with a 10 second immersion in 7:1 BHF followed by a water rinse (FIG. 6). Imaging at 365  $\mu\text{m}$  was also accomplished with this resist system using GCA 0.45NA step and repeat tool. A dose of 20 mJ/cm<sup>2</sup> was used for imaging (FIG. 7).

Although this invention has been described with respect to specific embodiments, the details thereof are not to be construed as limitations, for it will be apparent that various embodiments, changes and modifications may be resorted to without departing from the spirit and scope thereof, and it is understood that such equivalent embodiments are intended to be included within the scope of this invention.

We claim:

1. A process for generating a positive tone resist image on a substrate comprising the steps of:

- (a) coating the substrate with a radiation sensitive film comprising
  - (i) a film-forming aromatic polymer resin having functional groups which increase the chemical

reactivity of the resin towards electrophilic aromatic substitution,

- (ii) an acid catalyzable crosslinking agent comprising a carboxylate ester of a benzyl alcohol, which crosslinking agent forms an electron donating group stabilized benzyl carbonium ion upon reaction with acid, and
  - (iii) a radiation degradable acid generator which forms an acid upon exposure of said radiation sensitive film to imaging radiation, such that, upon crosslinking, said composition is rendered selectively less permeable to the absorption of an organometallic reagent in the crosslinked regions than it is in the non-crosslinked regions;
  - (b) imagewise exposing of the film to mid or deep UV radiation to cause crosslinking of the resin in the exposed portion of the film;
  - (c) contacting said film with an organometallic reagent to absorb the organometallic agent in more permeable unexposed areas; and,
  - (d) etching the film with reactive ions to yield a positive resist pattern.
2. The process of claim 1 wherein the organometallic reagent is in liquid or gaseous form.
3. The process of claim 2 wherein the organometallic reagent is selected from the group consisting of organosilicon, organotin, organogermanium and organotitanium compounds.
4. The process of claim 3 wherein the organometallic reagent is selected from the group consisting of dimethylaminotrimethylsilane, hexamethyldisilazane, trimethylsilyl chloride, trimethylstannyl chloride, and 1,1,3,3,5,5-hexamethylcyclotrisilazane.
5. The process of claim 1 wherein the functional groups of said aromatic polymer resin are phenolic hydroxy groups.
6. The process of claim 1 wherein the aromatic polymer resin is selected from the group consisting of poly(*p*-hydroxystyrene), poly(hydroxystyrene-co-*t*-butyloxycarbonyloxystyrene), poly(hydroxy-styrene-co-hydroxymethylstyrene), poly(hydroxystyrene-co-acetoxymethylstyrene), and novolak resin.
7. The process of claim 6 wherein the novolak resin is an alkylphenolformaldehyde condensation product.
8. The process of claim 7 wherein the alkylphenolformaldehyde condensation product is selected from the group consisting of cresol novolaks, ethylphenol novolaks, and xylene novolaks.
9. The process of claim 1 wherein said acid catalyzable crosslinking agent which forms a benzyl carbonium ion upon reaction with acid is a polyfunctional monomer.
10. The process of claim 9 wherein said polyfunctional monomer is selected from the group consisting of 2,6-diacetoxymethyl-*p*-cresol, 2,6-diacetoxy phenol 2,2',6,6'-tetraacetoxymethyl-Bisphenol A, and trisacetoxymesitylene.
11. The process of claim 1 wherein said acid catalyzable crosslinking agent which forms a benzyl carbonium ion upon reaction with acid is a polyfunctional polymer.
12. The process of claim 11 wherein said polyfunctional polymer selected from the group consisting of acetoxymethylstyrene and copolymers thereof.
13. The process of claim 12 wherein said polyfunctional polymer is a copolymer of *p*-hydroxystyrene and *p*-acetoxymethyl styrene where the molecular ratio of *p*-hydroxystyrene to *p*-acetoxymethyl styrene is about 4 to 1.

14. The process of claim 1 wherein the radiation degradable acid generator which is adapted to absorb imaging radiation is selected from the group consisting of metallic and nonmetallic onium salts and non-metallic sulfonic acid precursors which generate strong acids upon exposure to radiation.

15. The process of claim 14 wherein the onium salts are selected from the group consisting of diaryliodonium salts and triarylsulfonium salts.

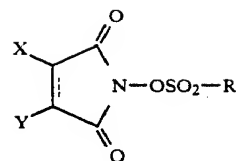
16. The process of claim 15 wherein the diaryliodonium salts are selected from the group consisting of diaryliodonium hexafluoroarsenates, hexafluoroantimonates, and triflates.

17. The process of claim 16 wherein the diaryliodonium hexafluoroarsenates, hexafluoroantimonates, and triflates are selected from the group consisting of diphenyliodonium hexafluoroarsenate, di(*t*-butylphenyl)iodonium hexafluoroarsenate, diphenyliodonium hexafluoroantimonate, di(*t*-butylphenyl)iodonium hexafluoroantimonate, diphenyliodonium triflate, and di(*t*-butylphenyl)iodonium triflate.

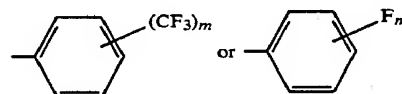
18. The process of claim 15 wherein the triarylsulfonium salts are selected from the group consisting of trialkylsulfonium hexafluoroantimonates, hexafluoroarsenates, hexafluorophosphates, and triflates.

19. The process of claim 18 wherein the trialkylsulfonium hexafluoroantimonates, hexafluoroarsenates, hexafluorophosphates, and triflates are selected from the group consisting of triphenylsulfonium hexafluoroantimonate, tri(*t*-butylphenyl) sulfonium hexafluoroantimonate, triphenylsulfonium hexafluoroarsenate, tri(*t*-butylphenyl)sulfonium hexafluoroarsenate, triphenylsulfonium hexafluorophosphate, tri(*t*-butylphenyl)sulfonium hexafluorophosphate, triphenylsulfonium triflate, and tri(*t*-butylphenyl)sulfonium triflate.

20. The process of claim 14 wherein the non-metallic sulfonic acid precursors are N-sulfonyloxyimides of the form



where R is selected from the group consisting of  $-\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_3$ ,  $-\text{CF}_2\text{CF}_2\text{H}$ ,  $-(\text{CF}_2)_n-\text{Z}$  where  $n=1$  to  $4$ , where Z is H, alkyl, aryl,



where  $m=1$  to  $5$ , where X and Y either (1) form a cyclic or polycyclic ring which may contain one or more hetero atoms, (2) form a fused aromatic ring, (3) may be independently H, alkyl or aryl, (4) may be attached to another sulfonyloxyimide-containing residue, or (5) may be attached to a polymeric chain or backbone.

21. The process of claim 1 which further includes an effective amount of an aromatic dye to absorb substantially all imaging electromagnetic radiation incident on said film during imaging.

22. The process of claim 21 wherein said aromatic dye is selected from the group consisting of nitrostilbene, substituted anthracenes, and substituted biphenyls.

23. The process of claim 22 wherein said anthracene is selected from the group consisting of phenoxymethyl anthracene, anthracene methanol, 9,10-diphenyl-anthracene, and phenanthracene.

\* \* \* \* \*

## Exhibit C



# Efficiency of Photoacid Generators in Chemically Amplified Resists for 157nm Lithography

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The photoacid generation efficiency of six photoacid generators was measured upon exposure to 157nm light in a candidate polymer for 157nm resist formulations of poly(NBHFA-co-NBTBE) using a standard addition technique. The photoacid generators studied were triphenylsulfonium perfluoro-1-butanefluorobutylsulfonate (TPS-Nf), bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-butanefluorobutylsulfonate (BBI-Nf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanefluorobutylsulfonate (NDI-Nf), and bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS). For the four ionic salts the photochemical efficiency was in the order BBI-Nf > BBI-Tf > BBI-PFOS > TPS-Nf. The photoacid generators NDI-Nf and TFMDNBS exhibited extremely poor efficiency for photoacid generation in this resist system under exposure to 157nm radiation.

**Keyword:** photoacid generator, triphenylsulfonium perfluoro-1-butanefluorobutylsulfonate, 157 nm lithography

## 1. Introduction

The continual increase in the speed and performance of microelectronic devices is a result of improvements to the resolution capabilities of photolithographic imaging since shrinking the size of transistors increases the speed of integrated circuits. The smallest printable feature into thin films of photoresist by an optical exposure system is directly proportional to the wavelength of light used in the exposure tool.<sup>1</sup> Decreasing the wavelength of the exposure source increases the resolution of the exposure system. Current state-of-the art lithographic processes use 193nm light to pattern features with dimensions less than 100nm.<sup>2</sup> To push resolution limits to smaller dimensions, the wavelength of the exposure source used in optical lithography will likely be reduced to 157nm in the coming years. As with previous generations of photolithography, the improvement in resolution afforded by reducing the wavelength of light used in the exposure system cannot be realized until a photoresist has been designed and optimized to function at that wavelength.

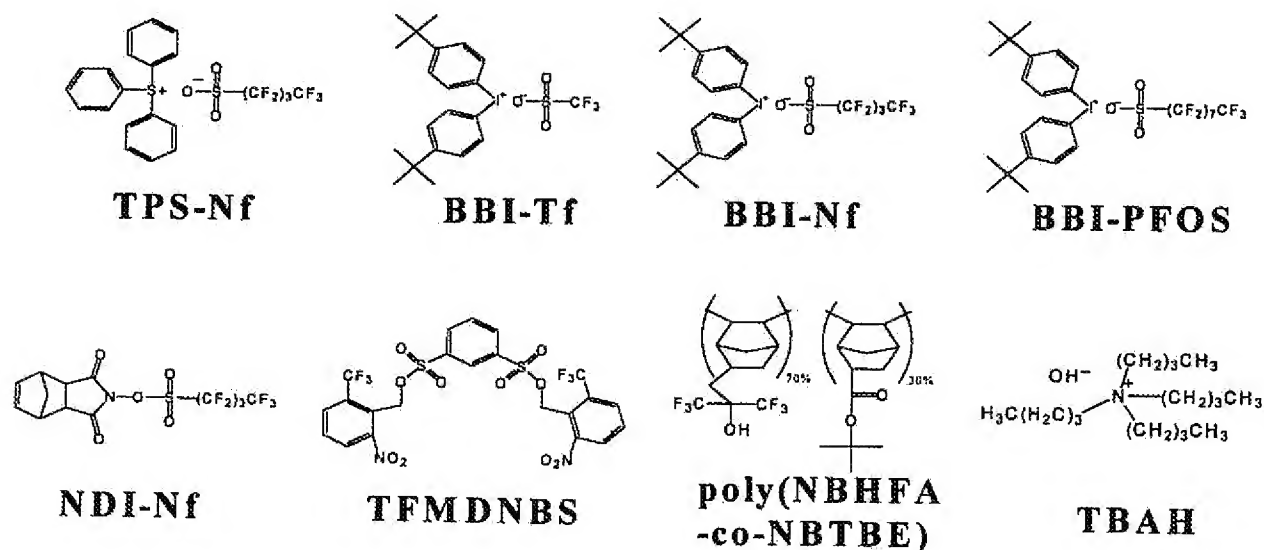
The extension of optical lithography into the vacuum ultraviolet (VUV) at 157nm has introduced tremendous challenges to the design of photoresist materials. At this wavelength organic materials absorb light strongly. The large attenuation of 157nm light through a resist film limits its usable thickness, and for most organic materials that are commonly used in photoresists, the film thickness is limited to less than about 150nm.<sup>3</sup> Another consideration in the design of 157nm photoresists is the energy of the exposure source. At 157nm (7.9eV) the photon energy becomes sufficiently large to excite, and possibly dissociate, common chemical bonds of polymer molecules used as the matrix of the resist.<sup>4,6</sup> These processes may serve to delocalize the photochemistry of the resist and lead to extensive radiation damage of the polymer. These factors should be considered for the design and optimization of 157nm resist formulations.

Single layer resist processes for 157nm lithography will likely use chemical amplification to boost resist sensitivity to exposure. A chemically amplified



photoresist uses the generation of a catalyst during exposure to perform chemical reactions within the resist matrix during a post-exposure bake that ultimately change the development rate of the exposed regions of the film. Chemical amplification is derived from the fact that one photogenerated molecule catalyzes numerous chemical reactions within the resist. The most common positive-tone chemically amplified photoresists rely on the generation of a strong photoacid by the decomposition of a photoacid generator (PAG) upon exposure to catalyze the removal of acid-labile protecting groups from the polymer. Photoacid catalyzes the deprotection of the polymer by a reaction-diffusion process within the resist matrix during a post-exposure bake (PEB). The removal of protecting groups increases the dissolution rate of the resist in a developing solution, typically aqueous base, and a pattern is formed by the difference in dissolution rates of the exposed and unexposed regions. The sensitivity of the resist (exposure dose required to develop) is therefore a combination of the efficiency of the decomposition of PAG to produce photoacid, the action of photoacid to deprotect the polymer, and the dissolution rate of the deprotected resist.

In this work, we measured the efficiency of photoacid generation for six PAGs in a candidate polymer for 157nm resist formulations using a standard addition technique. Details of the standard addition technique and its validation have previously been published.<sup>7</sup> In brief, the technique relies on the addition of a base quencher to the resist formulation that neutralizes a stoichiometric equivalence of photoacid generated by exposure. The exposure dose required to develop the resist increases as the base concentration increases since photoacid is neutralized. Experimental measurements of the dose to clear as a function of the added base concentration are fit using a model that describes the photoacid generation process and the neutralization of photoacid by base. The efficiency of photoacid generation is quantified by the resist C parameter,<sup>8</sup> a parameter that is proportional to the quantum yield of the photodecomposition of PAG to form photoacid. Once the C parameter is known, the concentration of photoacid can be calculated for any exposure dose. Of the six PAGs examined in this work, iodonium salts exhibited the greatest efficiency for photoacid generation, but required a greater concentration of photoacid than sulfonium salts to render development.



**Fig. 1.** Chemical structures for the resist materials used in this study: triphenylsulfonium perfluoro-1-butanefulfonate (TPS-Nf), bis(4-*tert*-butylphenyl) iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-butanefulfonate (BBI-Nf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanefulfonate (NDI-Nf), bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS), tetrabutyl ammonium hydroxide (TBAH), and the poly(NBHFA-co-NBTBE) polymer.

## 2. Experimental

The photoacid generators triphenylsulfonium perfluoro-1-butanesulfonate (TPS-Nf), bis(4-*tert*-butylphenyl)iodonium trifluoromethanesulfonate (BBI-Tf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-butanesulfonate (BBI-Nf), bis(4-*tert*-butylphenyl)iodonium perfluoro-1-octanesulfonate (BBI-PFOS), and N-hydroxy-5-norbornene-2,3-dicarboximide perfluoro-1-butanesulfonate (NDI-Nf) were purchased from Midori Kagaku Co. (Tokyo, Japan). The photoacid generator bis(2-trifluoromethyl-6-dinitrobenzyl) 1,3-benzene sulfonate (TFMDNBS) was provided by Agere Systems (Murray Hill, NJ). A copolymer of bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol (NBHFA) and bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*-butyl ester (NBTBE) was provided by International SEMATECH in collaboration with researchers at University of Texas at Austin. The composition of the polymer was 70% NBHFA and 30% NBTBE monomers. The average molecular weight was approximately 30,000 g/mol. The base quenchers, tetrabutyl ammonium hydroxide (TBAH) and 1-piperidineethanol (1PE) were purchased from Aldrich (Milwaukee, WI). TBAH was obtained as a 1M solution in methanol. Fig. 1 illustrates the chemical structures of the materials used in this study.

Resist solutions were formulated for each of the six PAGs in the poly(NBHFA-co-NBTBE) polymer from stock solutions of individual components. Stock solutions of PAG components were made in ethyl lactate, and the polymer was dissolved in propylene glycol methyl ether acetate (PGMEA). Stock solutions of TBAH and 1-PE were prepared by dilution with PGMEA. The concentration of PAG in each resist formulation was 100  $\mu$ mol/g resist based on solids content. For each PAG, a series of resist formulations was prepared that differed only in the concentration of base quencher. For TPS-Nf, two series of resist formulations were prepared using 1-PE and TBAH as the base quenchers. For all other PAGs only TBAH was used. The base concentration ranged from zero to 25  $\mu$ mol/g (0.0 to 0.25 ratio to the initial PAG concentration). Each resist solution was diluted to 5 wt% solids with PGMEA.

All samples were prepared on eight-inch silicon test wafers using a Polaris 2000 microlithography cluster

(FSI International). Substrates were coated with Shipley AR19-820 anti-reflective coating for a nominal thickness of 82.5 nm. Resist solutions were spin cast on top of the ARC and baked at 140°C for 60 seconds. Film thickness was controlled to yield an average film thickness of 125  $\pm$  5 nm. The optical constants (*n* and *k*) for resist films were determined from measurements on a vacuum ultraviolet-variable angle spectroscopic ellipsometer (VUV-VASE) (JA Woollam Co., Inc.) using silicon substrates without ARC. Exposures were performed using a 157nm microstepper (Exitech Limited). A 10x10 dose array was exposed on each sample without a mask (open frame). The post-exposure bake (PEB) for exposed resist samples was 110°C for 60 seconds for all resists except the TFMDNBS series for which the PEB was increased to 130°C for 90 seconds. Resist films were then developed in Shipley LDD-26W (0.26N tetramethylammonium hydroxide) developer for 20 seconds. The minimum exposure dose required to completely dissolve the resist film after development (dose to clear) was recorded for each sample.

## 3. Results

### A. Resist absorption in the vacuum ultraviolet

Table 1 lists the average absorption coefficients (base *e*) for the poly(NBHFA-NBTBE) polymer and six resist formulations. The absorption coefficients for the resist formulations were greater than for the polymer alone. The absorbance of the sulfonium resist was larger than the three iodonium and the dicarboximide formulations. The absorbance of iodonium resists increased slightly as the size of the anion increased. The resist containing TFMDNBS exhibited the greatest transparency of the six resists. Within the error of replicate measurements, the absorbance did not change for formulations containing the base quencher TBAH.

Table 1. Resist absorption coefficients

Photoacid Generator	Absorption Coefficient ( $\mu\text{m}^{-1}$ )
poly(NBHFA-co-NBTBE)	9.55
TPS-Nf	10.89
BBI-Tf	10.31
BBI-Nf	10.45
BBI-PFOS	10.70
ND-Nf	10.13
TFMDNBS	10.11

## B. Measurement of Dose to Clear Values for Resist Systems Containing Base Quenchers

The dose to clear was measured for a resist system consisting of the TPS-Nf PAG in poly(NBHFA-co-NBTBE) using the base quencher IPE. Two post-exposure bake conditions at 110°C for 60 seconds and 130°C for 60 seconds were used. As the concentration of base was increased, the dose to clear remained constant at values of 3.5 mJ/cm<sup>2</sup> and 1.05 mJ/cm<sup>2</sup> for the two PEB processes at 110°C and 130°C, respectively. Surprisingly, the IPE base quencher did not appear to neutralize photoacid within the resist. These effects were not explored further, and the IPE base quencher was not used in additional formulations.

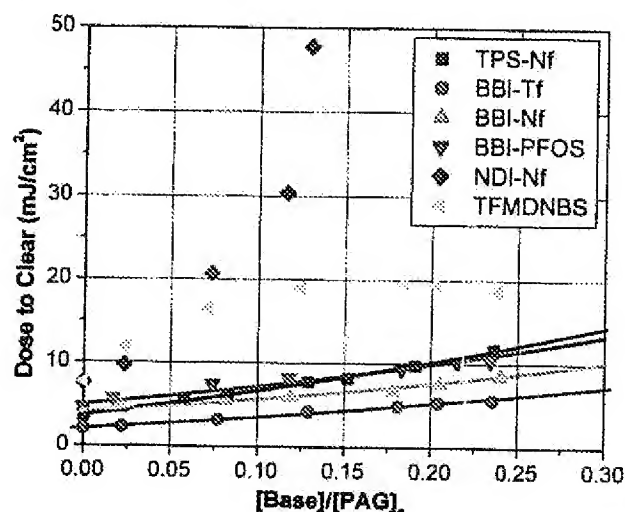


Fig. 2 Dose to clear values as a function of the ratio of base quencher to the initial PAG loading.

Using TBAH as the base, the dose to clear was measured for each series of resist formulations containing the six different PAGs. A PEB process was at 110°C for 60 seconds for each series except TFMDNBS in which the PEB temperature was increased to 130°C and baked for 60 seconds. In Fig. 2 the dose to clear for each system is plotted as a function of the added base concentration. The dose to clear values increased as the concentration of base quencher increased for resists containing sulfonium and iodonium salts. The dose to clear values for resists containing NDI-Nf increased rapidly for small additions of base quencher and as the concentration of base increased above 13  $\mu$  mol/g (0.13 [Base]/[PAG]<sub>0</sub>) the resist formulations did not develop, even for very large exposure doses above 100 mJ/cm<sup>2</sup>. The TFMDNBS

resist series exhibited a maximum in the dose to clear value at a concentration of base of approximately 15  $\mu$  mol/g (0.15 [Base]/[PAG]<sub>0</sub>), and then decreased slightly as additional base was added.

## 4. Discussion

### A. Resist Absorbance in the Vacuum Ultraviolet

As expected by the strong absorbance of phenyl groups in the VUV,<sup>3,4</sup> the absorbance of the resist formulations appeared to increase with increasing phenyl content. As follows, the sulfonium PAG increased the resist absorbance more than the iodonium PAG. Accordingly, the incorporation of sulfonium or iodonium PAGs to poly(NBHFA-co-NBTBE) increased the absorption coefficient to a greater degree than the NDI-Nf PAG. The exception to this trend appeared to be the resist containing TFMDNBS, as the absorbance of this resist was lower than the other five. The incorporation of fluorinated groups on carbonaceous materials is known to decrease the absorption of light in the VUV.<sup>9-11</sup> The presence of the fluorinated groups on this PAG likely decreased its contribution to the overall absorption of light by the resist. Contrary to this observation, the absorption coefficient of the iodonium resists slightly increased with increasing size of fluorinated alkyl anions.

### B. Base Quencher Selection

For the resist series containing the TPS-Nf PAG and the 1-PE base quencher the dose to clear did not increase as the concentration of base quencher increased. This suggested that the IPE base quencher did not act to neutralize photogenerated acid within the poly(NBHFA-co-NBTBE) resin. The IPE base quencher was previously validated and implemented with the standard addition technique in a matrix of poly(*p*-*t*-butoxycarbonyloxystyrene-co-*p*-hydroxystyrene) (PTBOCST).<sup>7,12</sup> In that work, the IPE base quencher was shown to neutralize photoacid and operate in accordance with the assumptions of the standard addition technique. No definite conclusions could be drawn from these observations, but IPE did not appear to function as a base quencher within the poly(NBHFA-co-NBTBE) copolymer.

It is important to note that the role of TBAH in the poly(NBHFA-co-NBTBE) has not been thoroughly examined nor proven to meet the assumptions of the

standard addition technique. The experiments used to evaluate 1-PE in PTBOCST cannot be easily applied to this resist system. Due to the strong absorbance of 157nm radiation by these resists, ultra-thin films of resist must be used. Measurements of the resist dissolution rate and infrared absorbance are difficult to perform in ultra-thin films. We recognize TBAH could effect resist performance beyond neutralization of photoacid, and these effects could lead to errors in the  $C$  parameter estimates. However, we believe that these effects will not alter the observed trends and will still permit characterization of the photoacid generators used in this work.

### C. Measurement of the Efficiency of Photoacid Generation Using the Standard Addition Technique

In accordance with the methods of the standard addition technique, the dose to clear for a resist system was measured as a function of the concentration of base quencher in the resist formulation.<sup>7</sup> Each formulation in

the series was prepared, exposed and developed under the same processing conditions. The efficiency of photoacid generation for the resist, described by the resist  $C$  parameter ( $\text{cm}^2/\text{mJ}$ ), was determined by fitting this experimental data to the standard addition model, written as

$$\langle A_{\text{Free}} \rangle = \frac{P_0}{x_0} \int_0^{x_0} 1 - \exp \{ -CD_0 e^{-\alpha x} \} dx - B \quad (1)$$

where  $A_{\text{Free}}$  ( $\mu\text{mol/g}$ ) is the free acid concentration,  $P_0$  ( $\mu\text{mol/g}$ ) is the initial concentration of PAG,  $x_0$  ( $\mu\text{m}$ ) is the film thickness,  $\alpha$  ( $\mu\text{m}^{-1}$ ) is the absorption coefficient of the resist,  $D_0$  ( $\text{mJ}/\text{cm}^2$ ) is the dose to clear value, and  $B$  ( $\mu\text{mol/g}$ ) is the concentration of base quencher. Assuming that at each value of the dose to clear the free acid concentration is equivalent, experimental data for the dose to clear as a function of the base quencher concentration was fit to eq. (1) by nonlinear minimization to determine the values of the  $C$  parameter and the free acid concentration.

Table 2. Calculated values for the resist  $C$  parameter and free acid concentration

Photoacid Generator	$C$ Parameter ( $\text{cm}^2/\text{mJ}$ )	Free Acid Concentration ( $\mu\text{mol/g}$ )	Sensitivity ( $\text{mJ}/\text{cm}^2$ )
TPS-Nf	0.077 (0.071,0.084)	142 (124,162)	3.7
BBI-Tf	0.170 (0.140,0.199)	17.6 (13.4,21.8)	2.1
BBI-Nf	0.204 (0.118,0.290)	36.4 (23.0,49.8)	3.9
BBI-PFOS	0.124 (0.062,0.186)	28.9 (13.9,44.0)	4.6
NDI-Nf	0.02 estimated	—	7.6
TFMDNBS	0.01 estimated	—	7.6

95% Confidence intervals are shown in parentheses

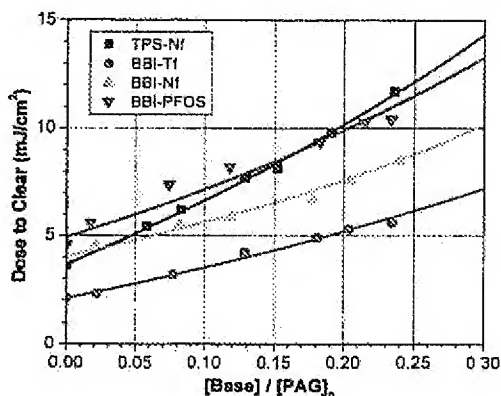


Fig. 3 Experimental data and model predictions for ionic salt PAGs

The experimental data for the sulfonium and iodonium PAGs were fit to eq. (1) by non-linear minimization using Mathematica (Wolfram Research). Table 2 lists the values of the extracted parameters and their 95% confidence intervals. The experimental data and best-fit solutions for the ionic salts are shown in Fig. 3. The model was unsuccessful in predicting reasonable parameter estimates for the NDI-Nf and TFMDNBS PAGs. Results for the various PAGs are discussed in the following sections.



#### D. Comparison of Sulfonium and Iodonium Salt Photoacid Generators

The sensitivity of photoresist is often characterized by its dose to clear. A resist with a low dose to clear exhibits a good sensitivity. Table 2 tabulates the dose to clear value at zero loading of base quencher for each photoacid generator. For the iodonium salts the dose to clear increased with increasing length of the PAG anion. This decrease in sensitivity was expected due to diffusion of the photoacid through the polymer. Increasing the size of the anion was expected to decrease the diffusion coefficient of the acid. Additional acid was required to complete sufficient deprotection of the polymer during the PEB, increasing the dose to clear.

The values of the *C* parameter calculations using the standard addition technique are presented in Table 2. The photoacid generation efficiency for the ionic salts was determined to be in the order BBI-Nf > BBI-Tf > BBI-PFOS > TPS-Nf. TPS-Nf was found to be much less efficient at generating photoacid than the iodonium salts. Since the difference in efficiency between TPS-Nf and the iodonium salts is much greater than the differences among the various iodonium compositions, it is likely that sulfonium salts containing similar anion variations would likewise be less efficient than their iodonium counterparts.

The lower efficiency for photoacid generation for BBI-PFOS as compared to BBI-Tf and BBI-Nf was not understood. Solution-based experiments of triphenylsulfonium salts exposed to deep ultraviolet radiation found that the composition of the anion can affect the overall efficiency and product distributions during PAG photolysis.<sup>13</sup> Strong nucleophilic anions were shown to reduce the total generation of acid by interfering with reactive intermediates. We do not expect this process to be important in these resist systems since the length of the fluorocarbon chain only mildly affects the nucleophilic strength of the anion and a trend with chain length was not observed. Previous work using the standard addition method measured a greater *C* parameter for a resist containing BBI-PFOS as compared to a BBI-Tf formulation in a phenolic resin when exposed to 248nm light.<sup>14,15</sup> The same resist formulations displayed the opposite trend, where BBI-Tf was more efficient than BBI-PFOS, when exposed to 157nm and ionizing forms of radiation (extreme ultraviolet, x-ray,

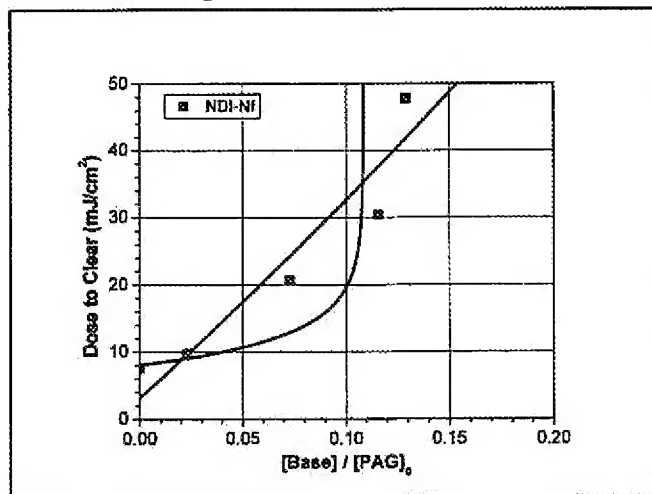
and e-beam).<sup>15</sup> The experimental results of the present study qualitatively agree with those from previous work.

Direct comparisons of the free acid concentration required to develop resists may be made since all processing conditions were equivalent for each PAG. The required free acid concentration of the TPS-Nf resist was lower than all the iodonium formulations, including BBI-Tf. This was surprising since the acid generated by BBI-Tf, triflic acid, is smaller than the molecule of perfluorobutane sulfonic acid generated from TPS-Nf. Based on diffusion arguments, a smaller acid should more readily diffuse through the resist film during the PEB. The increased concentration of photoacid required to develop formulations containing iodonium PAG may be related to dissolution inhibition. Strong dissolution inhibitors may increase the required extent of deprotection to achieve the same development rate, increasing the required free acid concentration. Additionally, the diffusivity of the photoacid may be affected by the chemical composition of PAG or photodecomposition products if these species alter the physical properties of the resist film. Small differences in the density, glass transition temperature, or concentration of residual casting solvent may alter the diffusion of small molecules within the resist. Further investigation is required to determine if any of these processes were in effect.

The free acid concentration required for development for the resists containing iodonium PAGs was determined to follow the order BBI-Nf > BBI-PFOS > BBI-Tf. The lesser concentration of free acid required by the BBI-Tf resist follows expectations based on diffusion. The slightly greater acid concentration required by the BBI-Nf resist as compared to the BBI-PFOS resist does not follow the expected trend. Since the confidence intervals of the calculations for the BBI-Nf and BBI-PFOS systems overlap, it is possible that these experiments cannot discern small differences between these photoacids with sufficient resolution. Alternatively, the lower concentration of acid found in the BBI-PFOS resist could be related to the photochemical processes that reduce its efficiency compared to the other iodonium PAGs. The results provided by these studies only allow speculation, and further investigation is required.

### E. Inefficient Photoacid Generation by Dicarboximide Photoacid Generators

Dose to clear values for the NDI-Nf resist system could not be measured above a concentration of base of  $13 \mu\text{mol/g}$ . For the dose to clear values that could be determined, the standard addition technique was applied to calculate the  $C$  parameter and free acid concentration for this system (Fig. 4). However, unsatisfactory results were obtained, and the model was unsuccessful at predicting the process of photoacid generation for this system. Since the exposure dose required to develop NDI-Nf resists under these conditions was large, it is plausible that radiation damage may be affecting resist development. Cross-linking of poly(hydroxystyrene) was found to occur during exposure to 157nm radiation at exposure doses less than  $50 \text{ mJ/cm}^2$ .<sup>16</sup> It is unknown if similar reactions occur in poly(NBHFA-co-NBTBE), however if such negative-tone reactions did exist, the required acid concentration to enable development would increase. Once sufficient damage has occurred, the resist film would then become completely insoluble in developer. This behavior may explain the inability to develop the NDI-Nf resist films above a concentration of base of  $13 \mu\text{mol/g}$ .



**Figure 4.** Parameter estimates for the NDI-Nf resist system. For the two cases, the  $C$  parameters and free acid concentrations (confidence intervals in parentheses) are  $0.0063$  ( $0.0020, 0.0105$ )  $\text{cm}^2/\text{mJ}$ ,  $1.1$  ( $-4.6, 6.9$ )  $\mu\text{mol/g}$ , and  $0.54$  ( $0.35, 0.74$ )  $\text{cm}^2/\text{mJ}$ ,  $89.1$  ( $84.6, 93.7$ )  $\mu\text{mol/g}$ , respectively.

A linear approximation was employed to estimate the order of magnitude of the  $C$  parameter. By using a linear fit to only the first two data points, the effects at high base concentration were avoided. We recognize that this linear approximation contains significant

uncertainty and has been shown in previous work to limit the accuracy of parameter estimations.<sup>15</sup> However, it was useful in this case to obtain an order of magnitude estimate of the  $C$  parameter. By the linear approximation, a  $C$  parameter of the order  $0.02 \text{ cm}^2/\text{mJ}$  was calculated, making the photodecomposition of NDI-Nf much less efficient than the sulfonium or iodonium salts during exposure to 157nm radiation.

Previous work using the standard addition technique in phenolic polymers found the photochemical efficiency of another dicarboximide PAG, N-hydroxy-5-norbornene-2,3-dicarboximide trifluoromethanesulfonate (NDI-Tf), to be comparable to sulfonium and iodonium salts of the same anion.<sup>15</sup> The dramatic decrease in the efficiency of the dicarboximide PAG with respect to the ionic PAGs found in this study was attributed to the composition of the polymer. In a resist film, the polymer generally composes greater than 90% of the film. The interaction of radiation with the polymer and its subsequent energy transfer or chemical dissociation to form radicals was expected to greatly affect the photochemistry of PAG in the resist. The incorporation of fluorine into the polymer is known to increase transparency of the resin.<sup>9-11</sup> Additionally, the  $\sigma$  molecular orbital is greatly stabilized by the substitution of fluorine for hydrogen. This stabilization increases the binding energy of the C-F bond as compared to a C-H bond. The combination of these effects may reduce the transfer of energy from the polymer to the PAG or the production of radicals along the polymer backbone. The large increase in photochemical efficiency for the dicarboximide PAGs within phenolic matrixes as compared to poly(NBHFA-co-NBTBE) suggests such processes are important for acid generation by this class of PAG. This suggests that the direct photolysis of the dicarboximide PAG was not the primary mechanism for photoacid generation, and the reaction pathway depends on energy transfer from the matrix.

### F. Inefficient Photoacid Generation in Resists Containing TFMDNBS

Dose to clear measurements for the TFMDNBS system were first attempted using a post-exposure bake temperature of  $110^\circ\text{C}$ , however the dose to clear value without added base was in excess of  $15 \text{ mJ/cm}^2$ . To avoid extremely high doses that were expected to be

necessary to develop solutions at high base concentration, the PEB temperature was raised to 130°C. Since the post-application bake was 140°C, no complications were expected at this elevated temperature. As shown in Figure 2 the TFMDNBS resist series reached a maximum in the dose to clear at high levels of base. This behavior cannot be explained by the photoacid generation model described in eq. (1). It follows from the exposure kinetics that the dose to clear the resist film should always increase with increasing base concentration since base neutralizes an equivalence of photogenerated acid. Adding complexity to the exposure model by considering the generation of multiple molecules of acid or competing reactions of PAG to generate species other than photoacid also cannot explain the decrease in dose. In either of these models the concentration of photoacid created during exposure will always increase with increasing dose. The cause of the decrease in the dose to clear at high loadings of base quencher remains unknown. Since the other PAGs screened in this study did not indicate this effect, and all systems were formulated from the same batch of polymer, we believe the TFMDNBS PAG is responsible for this behavior. By using a linear approximation the  $C$  parameter of the TFMDNBS system was calculated as approximately 0.01 cm<sup>2</sup>/mJ. Based on this estimation, the resist system containing the TFMDNBS PAG was inefficient at generating photoacid.

#### 4. Conclusions

The standard addition technique was used to evaluate the photochemical efficiency of six photoacid generators in a candidate polymer for 157nm lithography. Of the PAGs investigated, bis(*t*-butylphenyliodonium) salts exhibited the greatest efficiency for photoacid generation. Furthermore, the photochemical efficiency of triphenylsulfonium PAGs was approximately half that of bis(*t*-butylphenyliodonium) salts. Slight differences in the  $C$  parameter were determined for the iodonium salts containing different anions. Although consistent with previous studies, the source of these anion effects remains unknown. PAGs based on dicarboximide and on a fluorinated benzene sulfonate derivative were found to be extremely inefficient generators of photoacid at 157nm. For both of these systems, the model for photoacid generation from the decomposition of PAG upon exposure did not adequately explain the

experimental data. The free acid concentration required to develop the TPS-Nf resist was found to be less than the resist containing BBI-Tf, despite the much smaller photoacid molecule and identical processing conditions. These results suggest that the physical properties of photoresist may be affected by the composition of the PAG.

The sensitivity of a photoresist formulation to exposure radiation is a complex combination of the photochemical efficiency and the utilization of the free acid to drive polymer deprotection. Dose to clear values alone cannot indicate how these parameters interrelate. The standard addition model provides a useful tool for screening candidate materials by simultaneously determining these parameters using fast and simple experimental methods.

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#### References

1. Thompson, L. F., Willson, C. G., Bowden, M. J. & Editors. *ACS Symposium Series, Vol. 219: Introduction to Microlithography: Theory, Materials, and Processing* (1983).
2. Rahmani, M. D., et al., *Proc. SPIE-Int. Soc. Opt. Eng.* **4690**, 127 (2002).
3. Kunz, R. R. et al., *J. Vac. Sci. Technol. B* **17**, 3267-3272 (1999).

4. Murov, S. L., Hug, G. L. & Carmichael, I. *Handbook of photochemistry* (M. Dekker, New York, 1993).
5. Anderson, D. W. *Absorption of ionizing radiation* (University Park Press, Baltimore, 1984).
6. Becker, U, Shirley, D. A. "VUV and soft X-ray photoionization" (Plenum Press, New York, 1996).
7. Pawloski, A. R., Christian, Nealey, P. F., *Chem. Mater.* **13**, 4154-4162 (2001).
8. Dill, F. H., Hornberger, W. P., Hauge, P. S., Shaw, J. M., *IEEE Trans. Electron Devices* **ED22**, 445-52 (1975).
9. Robin, M. B., Ishii, I., McLaren, R. & Hitchcock, A. P., *J. Electron Spectrosc. Relat. Phenom.* **47**, 53-92 (1988).
10. Brundle, C. R., Robin, M. B., Kuebler, N. A., *J. Am. Chem. Soc.* **94**, 1466-75 (1972).
11. Brundle, C. R., Robin, M. B., Kuebler, N. A., Basch, H., *J. Am. Chem. Soc.* **94**, 1451-65 (1972).
12. Pawloski, A. R., Christian, Nealey, P.F., *Chem. Mater.* **14**, 4192-4201(2002).
13. Dektar, J. L., Hacker, N. P., *J. Am. Chem. Soc.* **112**, 6004-15 (1990).
14. Szmanda, C. R. et al., *J. Vac. Sci. Technol., B* **17**, 3356-3361 (1999).
15. Pawloski, A. R., Szmanda, C. R., Nealey, P. F., *Proc. SPIE-Int. Soc. Opt. Eng.* **4345**, 1056 (2001).
16. Fedynyshyn, T. H., Kunz, R. R., Sinta, R. F., Goodman, R. B., Doran, S. P., *J. Vac. Sci. Technol., B* **18**, 3332-3339 (2000).